

Dipole Moments and Intermolecular Interactions

Although the forces that hold molecules and solids together dominate the study of matter, there are other forces that affect chemical and physical properties. These are forces that arise as a result of the interactions between complete molecular units. Matter is composed of electrically charged particles, so it is reasonable to expect that there exists *some* force between any two molecules in close proximity.

Forces between molecules are of several types. Some compounds consist of polar molecules that attract each other as a result of the electrical charges. Other compounds consist of nonpolar molecules, but the electrons in one molecule are weakly attracted to the nuclei in another as a result of instantaneous electron distributions that are not symmetrical. Still other molecules contain hydrogen atoms that are attached to other atoms having high electronegativity, which leaves the hydrogen with a residual positive charge. As a result, the hydrogen atom can become attracted to an unshared pair of electrons on an atom in the same or another molecule. This type of interaction is known as hydrogen bonding. Although the forces that exist between molecules may amount to only 10 to 20 kJ mol⁻¹, they have a great influence on physical properties and in some cases chemical behavior. It is essential to have an understanding of these types of forces (sometimes called *nonchemical* or *nonvalence* forces) in order to predict and interpret the properties and behavior of inorganic compounds. This chapter is devoted to the subject of intermolecular interactions.

6.1 DIPOLE MOMENTS

Because atoms have different electronegativities, pairs of electrons that are shared in covalent bonds are not necessarily shared equally. The result is that the bond has a polarity with the center of negative charge generally residing on the atom having the higher electronegativity. For a covalent bond between two atoms, the dipole moment, μ , is expressed as

$$\mu = q \times r \quad (6.1)$$

where q is the quantity of charge separated and r is the distance of separation. In Chapter 3, the relationship between the dipole moment and the weighting coefficient of the ionic term in the molecular wave function for a diatomic molecule was determined. Several properties of molecules are

related to their polarity, and it is a useful parameter for understanding molecular structure, so it is appropriate to explore this topic in greater detail. Before doing so, a comment on units is appropriate. The charge on an electron is 1.6022×10^{-19} coulomb, and internuclear distances can be expressed in meters. As a result, the units on dipole moments are coulomb-meter (C m). A unit of polarity is defined as the *debye*, which is named after Peter Debye, who did pioneering work on polar molecules. The relationship in SI units is

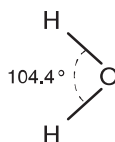
$$1 \text{ debye} = 1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

Historically (as well as currently by many chemists), the quantity of charge separated is expressed in electrostatic units, esu, which is $\text{g}^{1/2} \text{ cm}^{3/2} \text{ sec}^{-1}$. The charge on the electron is 4.80×10^{-10} esu, and when the internuclear distances are expressed in centimeters,

$$1 \text{ debye} = 1 \text{ D} = 10^{-18} \text{ esu cm}$$

Of course the results are identical in either set of units, but the latter units are somewhat more convenient for some purposes and will be used in this discussion.

For molecules that have several polar bonds, a rough approximation of the overall dipole moment can be made by considering the *bond moments* as vectors and finding the vector sum. Consider the water molecule, which has the structure



and for which the overall dipole moment is 1.85 D. If we consider that value to be the vector sum of the two O-H bond moments, we find that

$$1.85 \text{ D} = 2 \cos 52.25 \times \mu_{\text{O-H}} \quad (6.2)$$

Solving for $\mu_{\text{O-H}}$, we find a value of 1.51 D. We have another way to estimate the dipole moment of the O-H bond by making use of the equation

$$\% \text{ Ionic character} = 16 |\chi_A - \chi_B| + 3.5 |\chi_A - \chi_B|^2 \quad (6.3)$$

where χ_A and χ_B are the electronegativities of the atoms. By calculating the percent ionic character, we can determine the charge on the atoms. For an O-H bond,

$$\% \text{ Ionic character} = 16 |3.5 - 2.1| + 3.5 |3.5 - 2.1|^2 = 29.4\% \quad (6.4)$$

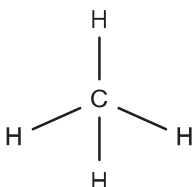
Therefore, because the length of the O-H bond is 1.10×10^{-8} cm (110 pm),

$$\mu_{\text{O-H}} = 0.294 \times 4.8 \times 10^{-10} \text{ esu} \times 1.10 \times 10^{-8} \text{ cm} = 1.58 \times 10^{-18} \text{ esu cm} = 1.58 \text{ D} \quad (6.5)$$

In this case, the agreement of the values calculated by the two methods is good, but it is not always so. One reason is that the simple vector approach ignores the effects of unshared pairs of electrons. Also, highly polar bonds can induce additional charge separation in bonds that might not otherwise

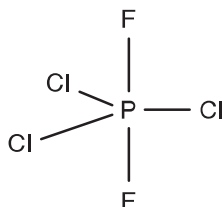
be polar. In some cases, bonds may be essentially nonpolar, as is the case for C–O and C–H bonds. Finally, many molecules are not adequately represented by a single structure because of resonance. As a result, the calculation of dipole moments for all but simple molecules is not a trivial problem.

The effect of molecular geometry can often be evaluated in a straightforward manner. Consider the tetrahedral CH_4 molecule, which will be shown as having one C–H bond pointing “up” and the other three forming a tripod-like base:



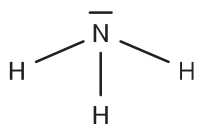
The bond pointing “up” constitutes one C–H bond in that direction while the other three must exactly equal the effect of one C–H pointing “down.” The “down” component of each of the three bonds can be obtained from $\cos(180 - 109^\circ 28') = 1/3$. Therefore, the three bonds exactly equal the effect of the one bond pointing in the “up” direction. This would be true for any regular tetrahedral molecule, so the dipole moment would be zero.

In Chapter 4, it was discussed that peripheral atoms of high electronegativity tend to bond to hybrid orbitals having a low degree of s character. In that connection, the molecule PCl_3F_2 is nonpolar indicating that the structure of the molecule is

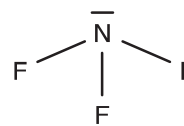


The axial orbitals used by phosphorus in this molecule can be considered as dp in character (see Chapter 4), which means they have no s character, whereas the orbitals in equatorial positions are sp^2 hybrids. As expected, the fluorine atoms are found in axial positions and the molecule is nonpolar. This illustration shows the value of dipole moments in predicting the details of molecular structure. Table 6.1 shows dipole moments for a large number of inorganic molecules.

One of the interesting aspects of dipole moments for molecules is seen when the molecules NH_3 and NF_3 are considered:



Bond angle: 107°
Dipole moment: 1.47 D



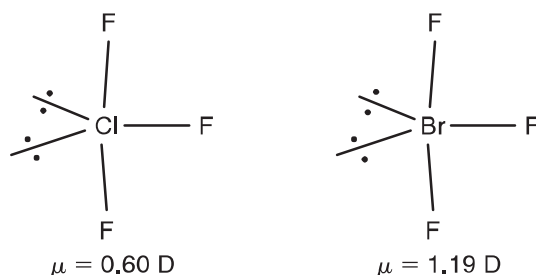
Bond angle: 102°
Dipole moment: 0.23 D

Table 6.1 Dipole Moments for Some Inorganic Molecules.

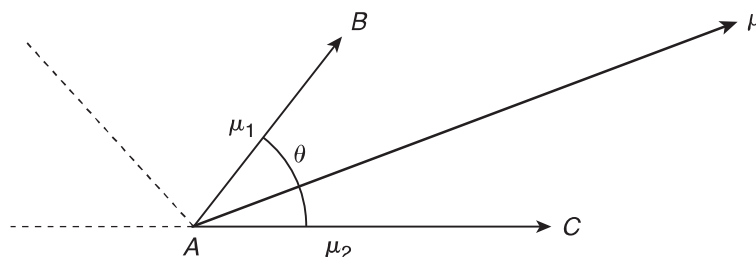
Molecule	Dipole Moment, D	Molecule	Dipole Moment, D
H ₂ O	1.85	NH ₃	1.47
PH ₃	0.58	AsH ₃	0.20
SbH ₃	0.12	AsCl ₃	1.59
AsF ₃	2.59	HF	1.82
HCl	1.08	HBr	1.43
HI	0.44	SOCl ₂	1.45
SO ₂ Cl ₂	1.81	SO ₂	1.63
PCl ₃	0.78	F ₂ NH	1.92
OPF ₃	1.76	SPF ₃	0.64
SF ₄	0.63	IF ₅	2.18
HNO ₃	2.17	H ₂ O ₂	2.2
H ₂ S	0.97	N ₂ H ₄	1.75
NO	0.15	NO ₂	0.32
N ₂ O	0.16	PFCl ₄	0.21
NF ₃	0.23	ClF ₃	0.60

For these two molecules, the structures are quite similar, and with the electronegativities of the atoms being N = 3.0, H = 2.1, and F = 4.0, even the polarities of the bonds are similar. The large difference in dipole moment is caused by the fact that in NH₃ there is a considerable effect produced by the unshared pair of electrons that causes the negative end of the dipole to lie in that direction. The N–H bonds are polar, with the positive ends lying in the direction of the hydrogen atoms. Therefore, the effect of the polar bonds adds to the effect of the unshared pair of electrons, giving rise to a large dipole moment. In NF₃, the unshared pair of electrons gives a negative charge to that region of the molecule, but because the fluorine atoms have higher electronegativity than the nitrogen atom, the negative ends of the polar N–F bonds lie toward the fluorine atoms. Thus, the unshared pair of electrons and the polar N–F bonds act in opposition to each other, which results in a low dipole moment for the NF₃ molecule.

The dipole moments of ClF₃ and BrF₃ provide another interesting illustration of the effects of unshared pairs of electrons. The molecules can be shown as follows:



Bond	Moment, D	Bond	Moment, D
H-O	1.51	C-F	2.0
H-N	1.33	C-Cl	1.47
H-S	0.68	C-Br	1.4
H-P	0.36	C-O	0.74
H-C	0.40	C=O	2.3
P-Cl	0.81	C-N	0.22
P-Br	0.40	C=N	0.9
As-F	2.0	C≡N	3.5
As-Cl	1.6	As-Br	1.3



■ **FIGURE 6.1** The vector model used to calculate dipole moments from bond moments.

Owing to the difference in electronegativities, the Br-F bonds are more polar than are the Cl-F bonds. However, the unshared pairs in ClF_3 are held closer to the Cl atom and the polarity of the Cl-F bond is in the opposite direction as the resultant of the two unshared pairs of electrons. In BrF_3 , the equatorial Br-F bond is slightly more polar than a Cl-F bond, but the unshared pairs reside farther away from the Br atom. Therefore, there is a greater effect produced by the two unshared pairs of electrons in BrF_3 that dominates the polarity of the equatorial Br-F bond. The result is that the dipole moment of BrF_3 is about twice as large as that of ClF_3 .

In many cases, it is useful to have some way to approximate the polarity of a molecule or a portion of the molecule. For this purpose, knowing the polarity of specific bonds can provide an approach to the problem. Table 6.2 shows the bond moments for numerous types of bonds.

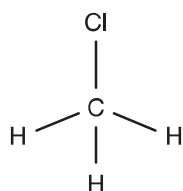
If the structure of a molecule and the bond moments are known, an approximate dipole moment can be obtained by treating the polar bonds as vectors. Figure 6.1 provides the vector diagram from which we obtain the resultant for two bonds as

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2 \mu_1 \mu_2 \cos \theta} \quad (6.6)$$

For molecules where the angle is obtuse (indicated by the dotted lines in Figure 6.1) the relationship is written as

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2 \mu_1 \mu_2 \cos (180 - \theta)} \quad (6.7)$$

If this approach is taken for the methyl chloride, CH_3Cl , molecule, which has the structure



the polarity of each C–H bond results in the negative end being toward the carbon atom. The resultant of the three C–H bonds added to the moment for the C–Cl bond gives the overall dipole moment for the molecule. It is found that each C–H bond is at $(180 - 109.5)^\circ = 70.5^\circ$ from a line directly opposite the C–Cl bond. Consequently, for three C–H bonds the result is

$$3 \mu_{\text{CH}} \times \cos 70.5 = 3 \mu_{\text{CH}} \times 0.33 = 1 \mu_{\text{CH}}$$

Therefore, the dipole moment for CH_3Cl is calculated to be

$$\mu_{\text{molecule}} = \mu_{\text{CH}} + \mu_{\text{CCl}} = 0.40 + 1.47 = 1.87 \text{ D}$$

For CClF_3 , the polarity of the three C–F bonds is in opposition to the C–Cl bond so that

$$\mu_{\text{molecule}} = \mu_{\text{CF}} - \mu_{\text{CCl}} = 2.00 - 1.47 = 0.53 \text{ D}$$

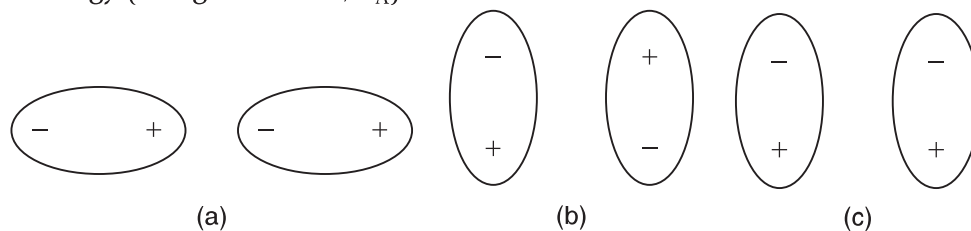
which is very close to the measured dipole moment of 0.50 D.

6.2 DIPOLE-DIPOLE FORCES

When two atoms having different electronegativities share a pair of electrons, the electrons are not shared equally. As a result, the bond between the atoms is said to be polar because the electrons will reside closer to the atom of higher electronegativity, giving it a negative charge. For a diatomic molecule, the dipole moment, μ , is given by

$$\mu = q \times r \quad (6.8)$$

and in Chapter 3, it was shown that HCl behaves as if 17% of the charge on an electron is transferred from H to Cl. For HF, the charge separation is 43% of the charge on the electron. When molecules having charge separations approach each other, there are electrostatic forces between them. Orientations such as those shown in Figures 6.2a and 6.2b that place opposite charges closer together represent lower energy (a negative value, E_A).



■ **FIGURE 6.2** Arrangements of dipoles. (a) and (b) lead to attraction (interaction energy negative) and (c) leads to repulsion (interaction energy positive).

An arrangement such as that shown in Figure 6.2c leads to repulsion (the energy is positive, E_R). Although it might be assumed that such an arrangement could not occur, this is not exactly true. It represents a higher energy state than those in which the orientations place opposite charges in close proximity, but the population of a state of higher energy is governed by the Boltzmann distribution law. For two states having energies defined by E_A and E_R as described earlier, the populations of the states (n_A and n_R) can be related to the energy difference between them, ΔE , by

$$\frac{n_R}{n_A} = e^{-\Delta E/kT} \quad (6.9)$$

where k is Boltzmann's constant, T is the temperature (K), and the other quantities were defined earlier. Therefore, although the repulsive state is higher in energy, it can have a small population depending on the temperature and ΔE . Because the population of the attractive state is larger, there is a net attraction between two polar molecules. The net energy between two dipoles that are restricted in orientation, E_D , is

$$E_D = -\frac{\mu_1\mu_2}{r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)] \quad (6.10)$$

In this equation, θ_1 , θ_2 , ϕ_1 , and ϕ_2 are the angular coordinates that describe the orientations of the polar molecules 1 and 2, μ_1 and μ_2 are their dipole moments, and r is the average distance of separation of the molecules. It should be noted that if two dipoles are restricted to fixed orientations in a solid, the energy varies as $1/r^3$ as shown earlier, and an energy expression containing that factor is frequently encountered. However, in a liquid the orientations change, and all orientations from the antiparallel attractive arrangement to the parallel repulsive arrangement are possible. There is some average orientation which is obtained by summing all of the possible orientations. When this is taken into account and the average orientation is used, the energy varies as $1/r^6$ and is expressed as

$$E_D = -\frac{2\mu_1^2\mu_2^2}{3r^6 kT} \quad (6.11)$$

If only one type of polar molecule is present, the interaction energy can be expressed as

$$E_D = -\frac{2\mu^4}{3r^6 kT} \quad (6.12)$$

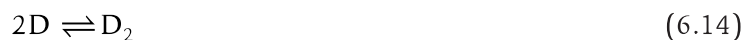
On a molar basis, the energy of interaction is given by

$$E_D = -\frac{2\mu^4}{3r^6 RT} \quad (6.13)$$

Although the association of polar molecules is accompanied by an energy change of only approximately 2 to 5 kJ mol^{-1} , the effect on physical properties is great.

It is important to keep in mind that the ability of dipoles to associate is influenced by their environment. Many studies on association of dipoles have been carried out in solutions containing the polar molecules. If the molecules of the solvent are polar or can have polarity induced in them (see Section 6.3), association of the solute molecules will be hindered. The solvent molecules will surround the polar solute molecules, which will inhibit their interaction with other solute molecules. The solute

molecules must be at least partially “desolvated” before association can occur. If we represent a polar molecule as D, the association reaction to form dimers can be written as



or, in a more general form where aggregates may contain n molecules, the reaction is



The equilibrium constants for these reactions may differ by as much as a factor of 10 to 100 depending on the nature of the solvent. If the solvent is a nonpolar one such as hexane, the interactions between the polar solute molecules are much stronger than are the interactions between solvent and solute. As a result, the equilibrium constant for dipole association will be large. On the other hand, if the solvent consists of polar molecules such as CH_3OH , the association of the solute molecules may be completely prevented owing to the interaction of polar solute molecules with the polar solvent molecules. The solute molecules must become partially “desolvated” in order to form dimers or larger aggregates. A solvent such as chlorobenzene or chloroform may not prevent association of polar molecules completely, but the equilibrium constant will almost always be smaller than it is when the solvent consists of nonpolar molecules such as hexane or CCl_4 .

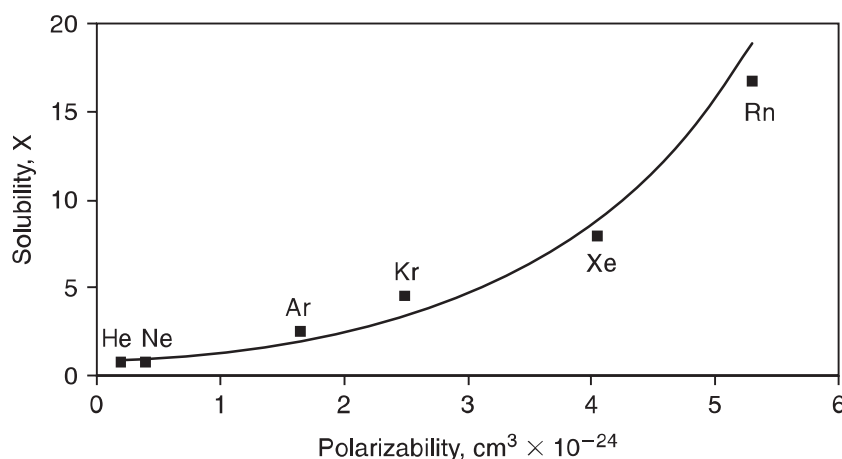
Although it does not strictly involve dipole association, an interesting case that illustrates the principles just described involves the association of lithium alkyls. For LiCH_3 , one of the stable aggregates is the hexamer, $(\text{LiCH}_3)_6$. In a solvent such as toluene, the hexamer units are maintained, but in a solvent like $(\text{CII}_3)_2\text{NCII}_2\text{CII}_2\text{N}(\text{CII}_3)_2$, which interacts strongly because of the unshared pairs of electrons on the nitrogen atoms, methyl lithium exists as a solvated monomer. As will be shown in Chapter 9, the association of electron donors and acceptors is also strongly affected by the ability of the solvent to interact with solute molecules.

6.3 DIPOLE-INDUCED DIPOLE FORCES

The electrons in molecules and atoms can be moved somewhat under the influence of a charge that generates an electrostatic force on the electrons. As a result, the electron cloud has some *polarizability*, which is represented as α . The total number of electrons may not be as important as the mobility of the electrons in determining the polarizability of a molecule. Consequently, molecules that have delocalized π electron systems generally have higher polarizabilities than do molecules having a similar number of electrons that are held in localized bonds. When a polarizable molecule having a spherical charge distribution approaches a polar molecule, a charge separation is induced in the molecule that was originally nonpolar. This interaction results in some force of attraction between the two species.

The polarizability of one molecule and the magnitude of the dipole moment of the other are the major factors that determine the strength of the interaction. The larger the dipole moment (μ) of the polar molecule and the higher the polarizability of the other molecule, the greater the strength of the interaction. Mathematically, the energy of the interaction of a dipole with a polarizable molecule can be expressed as

$$E_1 = -\frac{2\alpha\mu^2}{r^6} \quad (6.16)$$



■ **FIGURE 6.3** Solubility of noble gases in water as a function of polarizability.

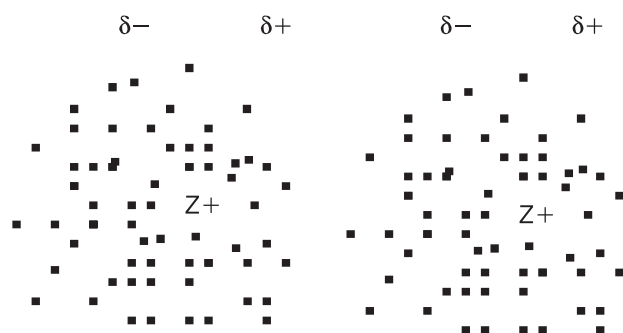
The interaction by dipole-induced dipole forces exists in addition to the London forces that cause an attraction even between molecules that are nonpolar. One of the most striking manifestations of dipole-induced dipole forces is that shown by the solubility of the noble gases in water. The greater the energy of interaction between the solute and solvent, the greater the solubility of the gas. Polar water molecules induce a charge separation in the noble gas molecules that increases with the polarizability of the noble gas. Accordingly, it would be expected that helium would interact very weakly with water and radon should interact more strongly in accord with their polarizabilities. Consequently, the solubility of the noble gases in water decreases in the order $\text{Rn} > \text{Xe} > \text{Kr} > \text{Ar} > \text{Ne} > \text{He}$, as is clearly shown graphically in Figure 6.3.

Another important consequence of dipole-induced dipole interactions is the difference in the solubility of oxygen and nitrogen in water. Expressed as grams of gas dissolved per 100 grams of water, the solubilities are 0.006945 and 0.002942, respectively, at 0°C . Both are nonpolar molecules, but the O_2 molecule has a greater polarizability. As a result, polar H_2O molecules cause a greater charge to be induced in the oxygen molecules, which results in stronger interactions with the solvent leading to greater solubility.

An important extension of these ideas is to cases where an ion interacts with polar molecules (ion-dipole forces). In such cases the polarity of the molecule is increased because of the inductive effect caused by the ion. Polar solvent molecules that surround an ion in the solvation sphere do not have the same polarity as do the molecules in the bulk solvent.

6.4 LONDON (DISPERSION) FORCES

In addition to the intermolecular forces that exist as a result of permanent charge separations in molecules, there must be some other type of force. Sometimes referred to as electronic van der Waals forces, they cause deviations from the ideal gas equation. These forces are not related to whether or not the molecules have a permanent dipole moment, but rather they exist between all molecules.



■ **FIGURE 6.4** An instantaneous distribution of electrons that leads to polarity in two atoms. There will be a force of attraction between the atoms (or molecules) even though they do not have permanent polarity. The number of electrons and their ability to be moved will determine the magnitude of the attractive force.

Otherwise, it would be impossible to liquefy substances such as CH_4 , O_2 , N_2 , and noble gases. The liquid and solid phases of many nonpolar compounds simply would not exist. We can see how such forces arise by considering two noble gas atoms that are in close proximity as shown in Figure 6.4. At some instant, the majority of electrons in one atom might be located on one side of the atom leaving the other half with an instantaneous positive charge. That charge can attract the electrons in another atom so that there is a net force of attraction between them. The result is an electron arrangement that can be called an *instantaneous dipole*. In 1929, Fritz London studied the forces that arise from this type of interaction, and they are called *London forces* or *dispersion forces*.

In order to arrive at a mathematical relationship to describe London forces, we will use an intuitive approach. First, the ability of the electrons to be moved within the molecule is involved. Atoms or molecules in which the electrons are highly localized cannot have instantaneous dipoles of any great magnitude induced in them. A measure of the ability of electrons in a molecule to be shifted is known as the electronic polarizability, α . In fact, each of the interacting molecules has a polarizability, so the energy arising from London forces, E_L , is proportional to α^2 . London forces are important only at short distances, which means that the distance of separation is in the denominator of the equation. In fact, unlike Coulomb's law, which has r^2 in the denominator, the expression for London forces involves r^6 . Therefore, the energy of interaction as a result of London forces is expressed as

$$E_L = -\frac{3h\nu_0\alpha^2}{4r^6} \quad (6.17)$$

where α is the polarizability, ν_0 is the zero point vibration frequency, and r is the average distance of separation between the molecules. The quantity $h\nu_0$ is the ionization potential, I , for the molecule. Therefore, the London energy can be represented by

$$E_L = -\frac{3I\alpha^2}{4r^6} \quad (6.18)$$

It is interesting to note that many different types of molecules have ionization potentials that do not differ greatly. Table 6.3 shows typical values for molecular ionization potentials for a wide variety of substances.

Table 6.3 Ionization Potentials for Selected Molecules.

Molecule	IP, eV	Molecule	IP, eV
CH ₃ CN	12.2	C ₂ H ₅ NH ₂	8.86
(CH ₃) ₂ NH	8.24	(CH ₃) ₃ N	7.82
NH ₃	10.2	HCN	13.8
H ₂ O	12.6	H ₂ S	10.4
CH ₄	12.6	CS ₂	10.08
HF	15.77	SO ₂	12.34
CH ₃ SH	9.44	C ₆ H ₅ SH	8.32
C ₆ H ₅ OH	8.51	CH ₃ OH	10.84
C ₂ H ₅ OH	10.49	BF ₃	15.5
CCl ₄	11.47	PCl ₃	9.91
AsH ₃	10.03	AsCl ₃	11.7
(CH ₃) ₂ CO	9.69	Cr(CO) ₆	8.03
C ₆ H ₆	9.24	1,4-Dioxane	9.13
<i>n</i> -C ₄ H ₁₀	10.63	OF ₂	13.6

1 eV is equivalent to 98.46 kJ/mol.

Because the ionization potentials are similar in magnitude, I can be replaced by a constant with no great effect on the value of E_L . The values of α for helium and argon are $2.0 \times 10^5 \text{ pm}^3$ and $1.6 \times 10^6 \text{ pm}^3$, respectively. Calculations show that for helium atoms separated by a distance of 300 pm (3 \AA), the energy of interaction is 76.2 J mol^{-1} , but the interaction of argon atoms at a distance of 400 pm (4 \AA) is 1050 J mol^{-1} . In agreement with the difference in these energies, solid argon melts at 84 K, whereas solid helium is obtained at 1.76 K at a pressure of 29.4 atmospheres. If we consider two nonpolar molecules such as CCl₄ ($\alpha = 2.6 \times 10^7 \text{ pm}^3$, b.p. 77°C) and C₆H₆ ($\alpha = 2.5 \times 10^7 \text{ pm}^3$, b.p. 80°C), we find that the polarizabilities are very nearly equal as are the boiling points. For these molecules, the interaction is only by London forces, so the comparison of boiling points and polarizabilities is valid.

In general, if the intermolecular forces are only of the London type, the boiling point (the temperature at which molecules of a liquid become separated from each other) will be higher the larger the molecule and the greater the number of electrons. For example, F₂ and Cl₂ are gases, Br₂ is a liquid, and I₂ is a solid at room temperature. The boiling points for GeCl₄ and SnCl₄ are 86.5°C and 114.1°C in accord with the difference in numbers of electrons and hence the polarizabilities. The increase in boiling point for the hydrocarbon series, C_{*n*}H_{2*n*+2} as n increases provides a familiar illustration of this principle.

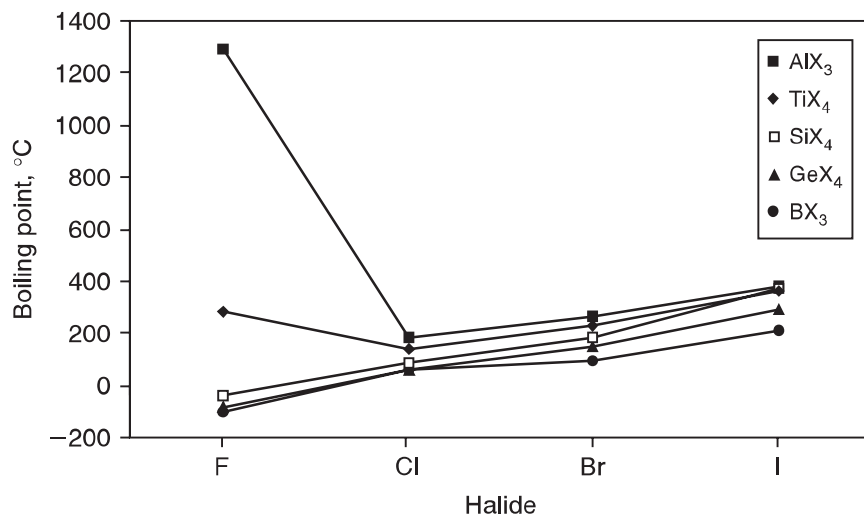
If two different types of molecules having polarizabilities α_1 and α_2 are interacting, the London energy between them can be expressed as

$$E_L = -\frac{3h\alpha_1\alpha_2}{2r^6} \cdot \frac{\nu_1\nu_2}{\nu_1 + \nu_2} = -\frac{3\alpha_1\alpha_2I_1I_2}{2r^6(I_1 + I_2)} \quad (6.19)$$

In Chapter 7, it will be pointed out that the bonding in solid silver halides is somewhat covalent. This results from the ions being polarizable so that the cation and anion have induced charge separations. For AgI, the electrostatic attraction is 808 kJ mol^{-1} , but the London attraction is 130 kJ mol^{-1} . From the examples presented, it is clear that London forces are significant enough to greatly affect the physical properties of compounds.

One of the consequences of increasing the number of electrons that accompanies an increase in molecular weight is that the London forces between molecules increase. The boiling points of a series of compounds composed of nonpolar molecules should reflect the greater force of attraction between molecules. To illustrate this trend, the boiling points of a series of organic compounds such as the hydrocarbons are considered. However, the trend is also well illustrated by numerous series of inorganic compounds. Figure 6.5 shows the boiling points of some of the halogen compounds of group IIIA and IV having the formulas EX_3 and EX_4 .

For those compounds, most of which consist of covalent molecules, there is the expected increase in boiling point with increasing molecular weight. The trigonal planar BX_3 and tetrahedral SiX_4 and GeX_4 compounds follow the expected trend as X progresses from F to I. Except for AlF_3 , the aluminum compounds are essentially covalent and exist as dimers, as do the aluminum alkyls, $[\text{AlR}_3]_2$, the structures of which were described in Chapter 4 and will be discussed further later in this chapter. However, there is a marked difference when AlF_3 is considered. In this case, the compound is essentially ionic, which results in a boiling point of approximately 1300°C . The total ionization potential to produce Al^{3+} is 5139 kJ mol^{-1} , so only in a case where there is a high lattice energy will the compound be ionic. Thus, the small size of the Al^{3+} and F^- allows them to form a lattice that is sufficiently stable to offset



■ FIGURE 6.5 Boiling points of group IIIA and IVA halides.

the high ionization energy required to produce Al^{3+} . The high boiling point for AlF_3 is a reflection of the different type of bonding present in that compound compared to the other aluminum halides. It is useful to remember that there is a continuum of bond character from covalent to ionic, and the bonding in AlF_3 is definitely toward the ionic end of the spectrum.

When a molecule dissolves in a liquid, some of the forces between the solvent molecules must be overcome. Unless an individual molecule of solute is considered, forces between the solute molecules must also be overcome. Effective solvation of solute molecules requires that the solute-solvent interactions lead to a favorable energy if the solute is to have significant solubility. Because nonpolar molecules interact as a result of the London forces between them, it should not be surprising to learn that compounds such as BI_3 that are nonpolar are soluble in nonpolar solvents such as CCl_4 and CS_2 . The polarizability of BI_3 is substantial owing to the large number of electrons contained in three iodine atoms, so the BI_3 molecules interact well with CCl_4 and CS_2 , both of which have relatively high polarizability. Likewise, AlBr_3 and AlI_3 are soluble in alcohol, ether, and carbon disulfide, whereas AlF_3 , which is composed of essentially nonpolarizable ions, is not.

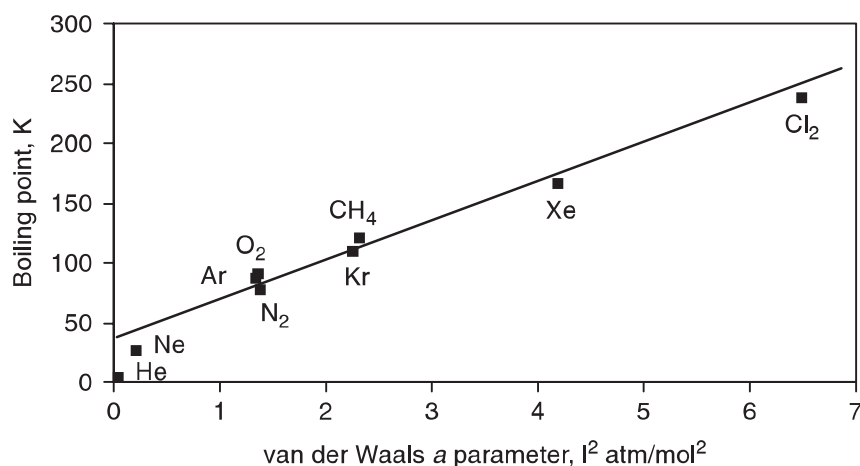
6.5 THE VAN DER WAALS EQUATION

In 1873, J. D. van der Waals recognized deficiencies in the ideal gas equation and developed an equation to eliminate two problems. First, the volume of the container is not the *actual* volume available to the molecules of the gas because the molecules themselves occupy some volume. The first correction to the ideal gas equation was to subtract the volume of the molecules from V , the volume of the container, to give the net volume accessible to the molecules. When modified to include the number of moles, n , the corrected volume is $(V - nb)$ where b is a constant that depends on the type of molecule.

From the ideal gas equation, it is found that for 1 mole of gas, $PV/RT = 1$, which is known as the *compressibility factor*. For most real gases, there is a large deviation from the ideal value, especially at high pressure where the gas molecules are forced closer together. From the discussions in previous sections, it is apparent that the molecules of the gas do not exist independently from each other because of forces of attraction even between nonpolar molecules. Dipole-dipole, dipole-induced dipole, and London forces are sometimes *collectively* known as van der Waals forces because all of these types of forces result in deviations from ideal gas behavior. Because forces of attraction between molecules reduce the pressure that the gas exerts on the walls of the container, van der Waals included a correction to the pressure to compensate for the “lost” pressure. That term is written as n^2a/V^2 , where n is the number of moles, a is a constant that depends on the nature of the gas, and V is the volume of the container. The resulting equation of state for a real gas, known as van der Waals’ equation, is written as

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad (6.20)$$

In van der Waals’ equation, it is the term n^2a/V^2 that is of interest in this discussion, because that term gives information about intermolecular forces. Specifically, it is the parameter a that is related to intermolecular forces rather than the number of moles, n , or the volume, V . It should be expected that the



■ FIGURE 6.6 Variation in boiling points of nonpolar molecules with van der Waals a parameter.

parameter a would show a correlation with other properties that are related to the forces between both organic and inorganic molecules.

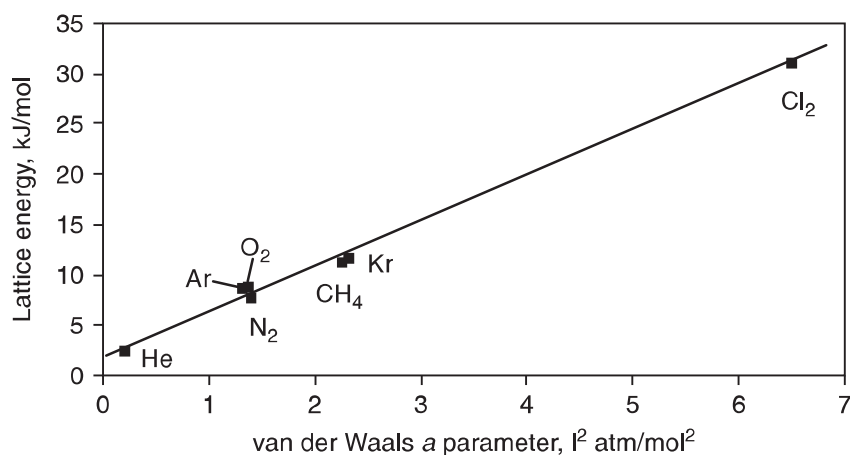
We will consider first a relatively simple case where the interactions between molecules are all of the same type (nonpolar molecules interacting as a result of London forces). For a liquid, the boiling point gives a measure of the strength of the forces between molecules in the liquid state because those forces must be overcome in order for the molecules to escape as a vapor. Figure 6.6 shows the boiling points of the noble gases and a few other substances as a function of the van der Waals a parameter.

It is apparent that for these nonpolar molecules the correlation is satisfactory. In this case, a characteristic of the liquid state (the boiling point) is correlated with a parameter from an equation that was developed to explain the behavior of gases. The liquid and gaseous states are referred to as *fluids*, and van der Waals' equation can be considered as an equation that applies to fluids as well as to gases through the use of the reduced variables (see references at the end of this chapter). Table 6.4 gives values for the van der Waals a parameter for molecules most of which are nonpolar.

Although a correlation between a property of a *liquid* and the a parameter in van der Waals' equation might be expected, we should remember that for nonpolar molecules the solid phase is also held together by London forces. Of course, the energy holding the solid together is the lattice energy so we should attempt a correlation of the lattice energy of solids composed of nonpolar molecules with the van der Waals a parameter. Such a correlation is shown in Figure 6.7, where the lattice energies of the noble gases and a few other nonpolar substances are plotted against a . It is immediately apparent that a linear relationship results, even though a property of a *solid* is being considered as a function of the parameter that results from considering the interaction of molecules of real gases.

The utility of the van der Waals a parameter should not be underestimated when physical properties of substances are being correlated and interpreted. Neither for that matter should the b parameter, because it is related to effective molecular dimensions, but that is not our concern in this chapter.

Table 6.4 Values for the van der Waals a Parameter for Selected Molecules.			
Molecule	a , liter ² atm/mol ²	Molecule	a , liter ² atm/mol ²
He	0.03412	C ₂ H ₆	5.489
H ₂	0.2444	SO ₂	6.714
Ne	0.2107	NH ₃	4.170
Ar	1.345	PH ₃	4.631
Kr	2.318	C ₆ H ₆	18.00
Xe	2.318	CCl ₄	20.39
N ₂	1.390	SiH ₄	4.320
O ₂	1.360	SiF ₄	4.195
CH ₄	2.253	SnCl ₄	26.91
Cl ₂	6.493	C ₂ H ₆	5.489
CO ₂	3.592	N ₂ O	3.782
CS ₂	11.62	GeCl ₄	22.60

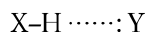


■ FIGURE 6.7 Variation in lattice energy of some nonpolar molecules with van der Waals a parameter.

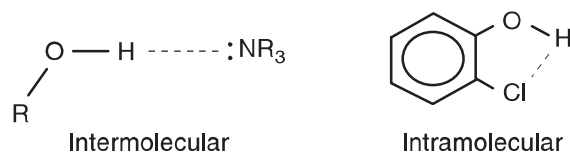
6.6 HYDROGEN BONDING

Thousands of articles and several books have been published on the subject of hydrogen bonding. It is a phenomenon that pertains to many areas of the chemical sciences, and it is an important type of molecular interaction. The fact that it is referred to as *hydrogen* bonding suggests that hydrogen is unique in this ability, and so it is. Of all the atoms, only hydrogen leaves a completely bare nucleus exposed when it forms a single covalent bond to another atom. Even lithium has a filled 1s level around the nucleus after the single electron in the 2s level is used in covalent bonding. When a

hydrogen atom is bonded to an element having an electronegativity of about 2.6 or higher (F, O, N, Cl, or S), the polarity of the bond is sufficient that the hydrogen carries a positive charge that enables it to be attracted to a pair of electrons on another atom. That attraction is known as a hydrogen bond (sometimes referred to as a hydrogen bridge). This type of interaction can be shown as



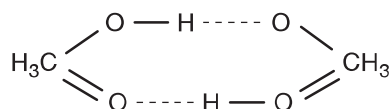
Hydrogen bonding occurs in many situations in chemistry. Materials such as proteins, cellulose, starch, and leather have properties that are the result of hydrogen bonding. Even solid materials such as NH_4Cl , $NaHCO_3$, NH_4HF_2 , and ice have strong hydrogen bonding between units. Water and other liquids that have OH groups on the molecules (e.g., alcohols) have extensive hydrogen bonding. There are two types of hydrogen bonds, which are illustrated by the following examples:



Both types of hydrogen bonds occur in pure liquids as well as in solutions. Many substances are associated at least partially in the vapor phase as a result of hydrogen bonding. For example, hydrogen cyanide is associated to give structures such as

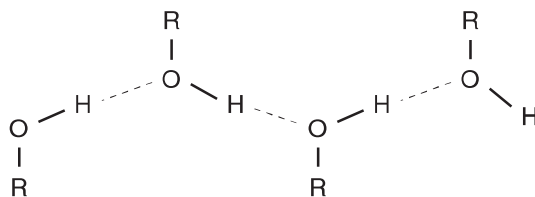


The association of acetic acid in the vapor phase occurs so that the molecular weight of the gas indicates that it exists as dimers:

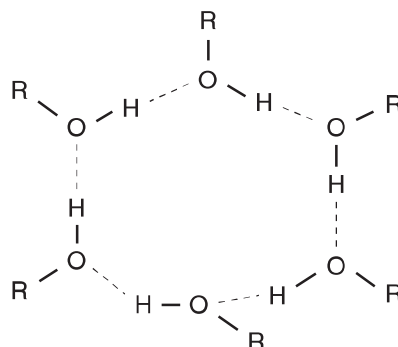


Studies have indicated that the association of HF in the gas phase leads predominantly to dimers or hexamers with small amounts of tetramers. Hydrogen bonding in liquids such as sulfuric and phosphoric acids is responsible for them being viscous liquids that have high boiling points.

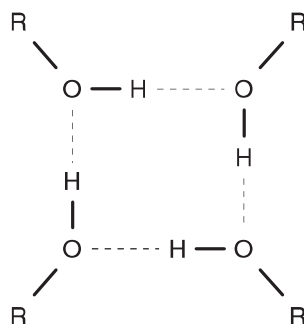
Association of alcohols in the liquid state occurs with the formation of several types of species including chains,



in which the O–H \cdots O bond distance is approximately 266 pm. The liquid also contains rings with the most predominant unit apparently being (ROH)₆, which can be shown as



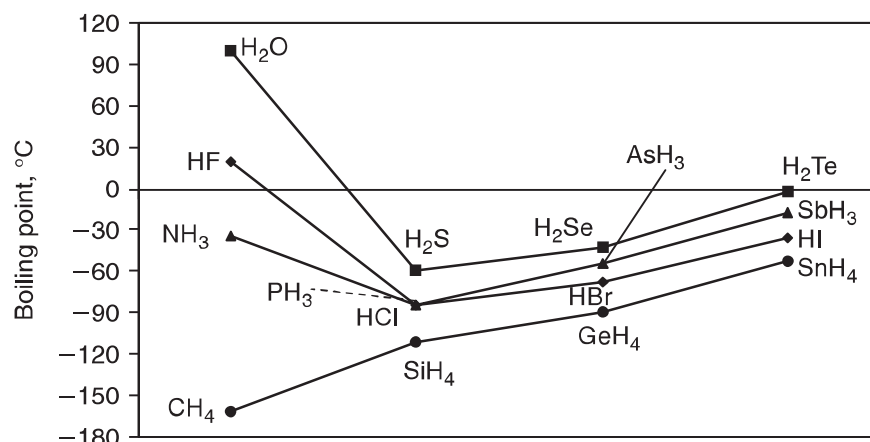
The vapor of CH₃OH also contains some cyclic tetramer, (CH₃OH)₄,



for which the heat of association has been found to be 94.4 kJ mol⁻¹ leading to a value of 23.6 kJ mol⁻¹ for each hydrogen bond. The equilibrium composition of alcohols in the vapor phase is temperature and pressure dependent. Boric acid, B(OH)₃, consists of sheetlike structures as a result of hydrogen bonding.

The body of information relating hydrogen bonding to physical properties is enormous. Only a brief summary will be presented, but more complete discussions can be found in the references cited at the end of this chapter. Perhaps the most familiar and elementary example of the effect of hydrogen bonding is reflected by the fact that the boiling point of water is 100 °C while that of liquid H₂S is -61 °C. Figure 6.8 shows the boiling points of the hydrogen compounds of the elements in groups IVA to VIIA.

There is no hydrogen bonding in the hydrogen compounds of the elements in group IV elements, so CH₄, SiH₄, GeH₄, and SnH₄ show the expected increase in boiling point with increasing molecular weight. For the hydrogen compounds of the group V elements, only NH₃ exhibits significant hydrogen bonding, so its boiling point (-33.4 °C) is clearly out of line with those of the other compounds (for example, PH₃ has a boiling point of -85 °C). Water shows clearly the effect of strong hydrogen bonds (in fact, multiple hydrogen bonds), which results in a boiling point of 100 °C for a compound that has a molecular weight of only 18. With the high electronegativity of fluorine, the polar H–F bond is susceptible to forming strong hydrogen bonds, as is clearly illustrated by the boiling point of HF being 19.4 °C while HCl boils at -84.9 °C.



■ **FIGURE 6.8** Boiling points of hydrides of groups IVA, VA, VIA, and VIIA.

It is also interesting to note that although the compounds have almost identical formula weights, the boiling point of BF_3 is -101°C while boric acid, $\text{B}(\text{OH})_3$, is a solid that decomposes at 185°C . Dimethyl ether and ethanol both have the formula $\text{C}_2\text{H}_6\text{O}$, but the boiling points are -25°C and 78.5°C , respectively. Hydrogen bonding between OH groups in alcohols leads to intermolecular forces that are not present in dimethyl ether.

When a liquid is changed into a vapor, the entropy of vaporization can be defined as

$$\Delta S_{\text{vap}} = S_{\text{vapor}} - S_{\text{liquid}} \cong S_{\text{vapor}} \cong \Delta H_{\text{vap}}/T \quad (6.21)$$

where T is the boiling point (in K). If the liquid is one in which London forces give the only type of interaction between molecules and the vapor is completely random, the entropy of vaporization can be represented as $\Delta H_{\text{vap}}/T$. The entropy of a mole of a random gas is approximately $88\text{ J mol}^{-1}\text{ K}^{-1}$, and the constant value for the entropy of vaporization of a liquid is known as *Trouton's rule*. Table 6.5 shows the data for testing this rule with a wide range of liquids.

For CCl_4 , the heat of vaporization is 30.0 kJ mol^{-1} and the boiling point is 76.1°C , which gives a value of ΔS_{vap} of $86\text{ J mol}^{-1}\text{ K}^{-1}$, a value that is in good agreement with Trouton's rule. On the other hand, the heat of vaporization of CH_3OH is 35.3 kJ mol^{-1} and the boiling point is 64.7°C . These values lead to a value for ΔS_{vap} of $104\text{ J mol}^{-1}\text{ K}^{-1}$. The deviation from Trouton's rule is caused by the fact that in the liquid state the molecules are strongly associated giving a structure to the liquid (lower entropy). Therefore, vaporization of CH_3OH leads to a larger entropy of vaporization than would be the case if the molecules of the liquid and vapor were arranged randomly.

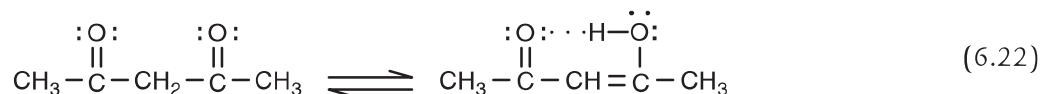
Acetic acid provides a different situation. The boiling point of acetic acid is 118.2°C and the heat of vaporization is 24.4 kJ mol^{-1} . These values yield an entropy of vaporization of only $62\text{ J mol}^{-1}\text{ K}^{-1}$. In this case, the liquid is associated to produce dimers as described earlier, but those dimers also exist in the vapor. Therefore, structure persists in the vapor so that the entropy of vaporization is much lower than would be the case if a vapor consisting of randomly arranged monomers were produced. It is interesting to note from the examples just described that a property such as the entropy of vaporization can provide insight as to the extent of molecular association.

Table 6.5 Thermodynamic Data for the Vaporization of Several Liquids.

Liquid	Boiling point, °C	ΔH_{vap} J mol ⁻¹	ΔS_{vap} J mol ⁻¹ K ⁻¹
Butane	-1.5	22,260	83
Naphthalene	218	40,460	82
Methane	-164.4	9,270	85
Cyclohexane	80.7	30,100	85
Carbon tetrachloride	76.7	30,000	86
Benzene	80.1	30,760	87
Chloroform	61.5	29,500	88
Ammonia	-33.4	23,260	97
Methanol	64.7	35,270	104
Water	100	40,650	109
Acetic acid	118.2	24,400	62

Other properties are also affected by hydrogen bonding. For example, the solubility of *o*-, *m*-, and *p*-nitrophenols (NO₂C₆H₄OH) are greatly different as a result of hydrogen bonding. The solubility of *p*-nitrophenol (which can hydrogen bond to a solvent such as water) in water is greater than that of *o*-nitrophenol, in which there is intramolecular hydrogen bonding. On the other hand, *o*-nitrophenol is much more soluble in benzene than is *p*-nitrophenol. The *ortho* isomer has intramolecular hydrogen bonds that allow the interaction of the solvent with the ring of the solute to be the dominant factor. As a result, *o*-nitrophenol is many times more soluble in benzene than is *p*-nitrophenol.

Hydrogen bond formation also leads to differences in chemical properties. For example, the enolization reaction of 2,4-pentadione (acetylacetone) is assisted by the formation of an intramolecular hydrogen bond:



In the neat liquid, the enol form is dominant, and in solutions the composition of the equilibrium mixture depends greatly on the solvent. For example, when the solvent is water, hydrogen bonding between the solvent and the two oxygen atoms can occur, which helps to stabilize the keto form that makes up 84% of the mixture. When the solvent is hexane, 92% of the acetylacetone exists in the enol form, in which intramolecular hydrogen bonding stabilizes that structure. Acetone undergoes only an extremely small amount of enolization (estimated to be less than 10⁻⁵%), which is at least partially the result of there being no possibility of hydrogen bonding in the enol form.

One of the most convenient ways to study hydrogen bonding experimentally is by means of infrared spectroscopy. When a hydrogen atom becomes attracted to an unshared pair of electrons on an atom

in another molecule, the covalent bond holding the hydrogen atom becomes weakened slightly. As a result, the absorption band that corresponds to the stretching vibration of the bond is shifted to a position that may be *lower* by up to 400 cm^{-1} . Because of the attraction between the hydrogen atom and a pair of electrons in another molecule, the bending vibrations of the covalent bonds holding the hydrogen atom are hindered. Therefore, the bending vibrations are shifted to *higher* frequencies. Although the hydrogen bond itself is weak, there is a stretching vibration for that bond that does not exist prior to the formation of the hydrogen bond. Because hydrogen bonds are weak, the stretching vibration occurs at very low wave numbers (generally $100\text{--}200\text{ cm}^{-1}$). All of these vibrations and the regions where they are found in the infrared spectrum are summarized in Table 6.6.

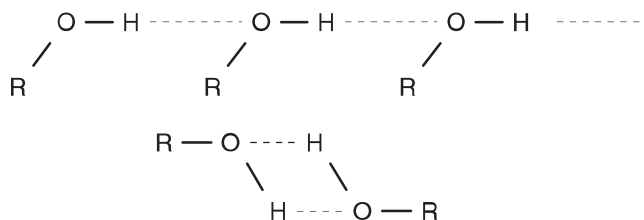
In very dilute solutions of CH_3OH in CCl_4 , the alcohol molecules are widely separated and the equilibrium



is shifted far to the left. The infrared spectrum of such a dilute solution shows a single band at 3642 cm^{-1} that corresponds to the “free” OH stretching vibration. As the concentration of alcohol is increased, other bands appear at 3504 and 3360 cm^{-1} that are due to higher aggregates that result from intermolecular hydrogen bonding between the OH groups as shown earlier. Figure 6.9 shows the spectra of 0.05 M , 0.15 M , and 0.25 M CH_3OH in CCl_4 solutions.

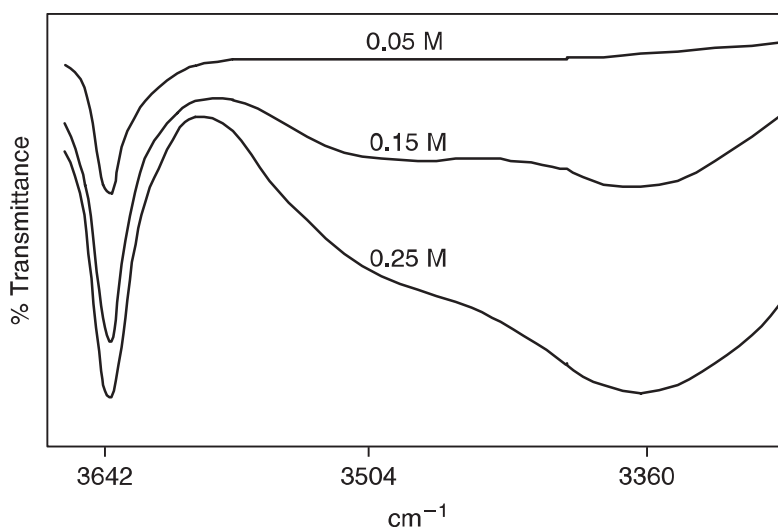
Table 6.6 Infrared Spectral Features Associated with Hydrogen Bonding.		
Vibration	Assignment	Spectral region, cm^{-1}
$\begin{array}{c} \leftarrow \rightarrow \\ \text{X}-\text{H} \cdots \text{B} \\ / \end{array}$	ν_s , the X–H stretch	3500–2500
$\begin{array}{c} \uparrow \\ \text{X}-\text{H} \cdots \text{B} \\ / \downarrow \end{array}$	ν_b , the in-plane bend ^a	1700–1000
$\begin{array}{c} \oplus \\ \text{X}-\text{H} \cdots \text{B} \\ / \oplus \end{array}$	ν_t , the out-of-plane bend ^b (torsion)	400–300
$\begin{array}{c} \leftarrow \rightarrow \\ \text{X}-\text{H} \cdots \text{B} \\ / \end{array}$	ν_s , the H \cdots B stretch ^c	200–100
^a Bending in the plane of the page. Hydrogen bonding causes higher ν_b . ^b Bending perpendicular to the plane of the page. Hydrogen bonding causes higher ν_t . ^c Stretching of the hydrogen bond to the donor atom. Increases with hydrogen bond strength.		

The spectra show that there are “free” OH groups at all concentrations, but the very broad peak at 3360 cm^{-1} shows a large fraction of the alcohol is bound in aggregates when the concentration is 0.25 M . In addition to the cyclic structures shown earlier, these aggregates are believed to have structures like the following:



As described earlier, there is doubtless a complex equilibrium that involves several species of aggregates having both chain and ring structures.

The effect of the solvent on equilibria involving molecular aggregation has been discussed in connection with dipole association. However, the nature of the solvent also has an effect on the position where the OH stretching band is observed in the infrared spectrum even though the OH group may not be involved in hydrogen bonding. The ability of the solvent to “solvate” the OH group affects vibrational energy levels even though the interaction is not actually considered to be hydrogen bonding. The absorption band due to the stretching vibration of the O–H bond in CH_3OH in the vapor phase is seen at 3687 cm^{-1} . In $n\text{-C}_7\text{H}_{16}$, CCl_4 , and CS_2 , the band is seen at 3649 , 3642 , and 3626 cm^{-1} , respectively. A hydrocarbon molecule has no unshared electron pairs to interact even weakly with the O–H bond, so the stretching vibration is at the highest position found in any of these solvents when $n\text{-C}_7\text{H}_{16}$ is the solvent. The band appearing at 3626 cm^{-1} when the solvent is CS_2 is indicative of very weak hydrogen bonding to the solvent in this case. When the solvent is benzene, the position of the OH stretching vibration for CH_3OH in a dilute solution is at 3607 cm^{-1} , indicating significant interaction of the OH group with the π -electron system of the benzene ring. Benzene is known to form complexes



■ **FIGURE 6.9** Infrared spectra for solutions of CH_3OH in CCl_4 .

with Lewis acids because of its ability to behave as a Lewis base (see Chapter 9). It is certainly not an “inert” solvent that should be chosen when hydrogen bonding studies are being carried out.

A relationship has been developed that relates the position of the O–H stretching band of an alcohol to the electronic character of the solvent. That equation is based on the assumption that an oscillating electric dipole is interacting with a solvent of dielectric constant ϵ . The equation can be written as

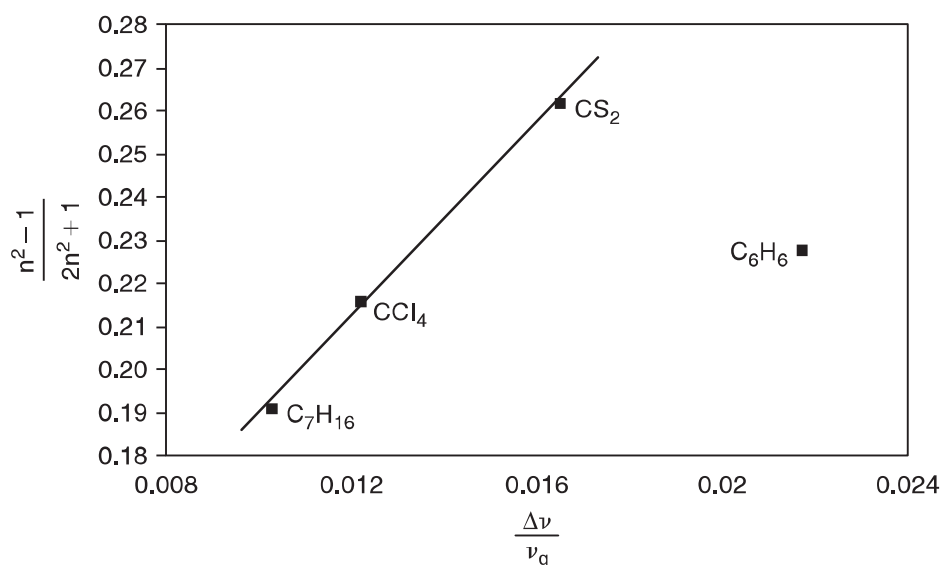
$$\frac{\nu_g - \nu_s}{\nu_g} = C \frac{\epsilon - 1}{2\epsilon + 1} \quad (6.24)$$

where ν_g and ν_s are the stretching frequencies in the gas phase and in solution and C is a constant. The dielectric constant at high frequency is usually approximated as the square of the index of refraction, n . When that is done, the shift in the position of the stretching band, $\Delta\nu = (\nu_g - \nu_s)$ is represented by the equation

$$\frac{\Delta\nu}{\nu_g} = C \frac{n^2 - 1}{2n^2 + 1} \quad (6.25)$$

which is known as the Kirkwood-Bauer equation. Figure 6.10 shows the correlation of the positions of the O–H stretching band of CH_3OH in heptane, CCl_4 , CS_2 , and benzene. The first three solvents appear to solvate CH_3OH in a “normal” manner and obey the Kirkwood-Bauer equation, but benzene is clearly interacting in a different way. As mentioned earlier, benzene is an electron donor that even forms complexes with metals. It is apparent from Figure 6.10 that benzene is by no means an “inert” solvent with regard to hydrogen bonding.

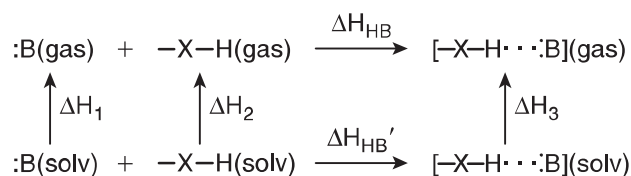
Hydrogen bond energies are sometimes described as weak, normal, or strong based on the strength of the bonds. Weak hydrogen bonds are those that are weaker than about 12 kJ mol^{-1} and are typical of the intramolecular hydrogen bond in 2-chlorophenol. Normal hydrogen bonds (which include



■ **FIGURE 6.10** A Kirkwood-Bauer plot showing the effect of solvent on the O—H stretching band of methanol in different solvents.

the vast majority of cases) are those which have energies of perhaps 10 to 40 kJ mol⁻¹. Typical of this type of bond are those that occur between alcohols and amines. The strong hydrogen bonds found in the symmetric bifluoride ion, [F ··· H ··· F]⁻, have a bond energy of approximately 142 kJ mol⁻¹. This ion has a distance between fluorine centers of 226 pm, so each bond is 113 pm, in accord with the bond order being 1/2. In this case, the strength of the hydrogen bonds is comparable to that of weak covalent bonds such as F-F, I-I, and the O-O bond in O₂²⁻.

Strengths of chemical bonds correspond to the bond enthalpies for molecules in the gas phase, and it is desirable to measure enthalpies of hydrogen bonding for that type of interaction. However, most hydrogen-bonded systems are not stable enough to exist at the temperatures required to vaporize the donor and acceptor. Therefore, strengths of hydrogen bonds are usually determined calorimetrically by mixing solutions containing the donor and acceptor. When the influence of the solvent is considered, as illustrated by the relationship shown in Eq. (6.25), the question arises as to whether the measured enthalpy is actually that of the hydrogen bond. The situation can be illustrated by means of a thermochemical cycle in which B is an electron pair donor and -X-H is the species that forms the hydrogen bond:



The actual strength of the hydrogen bond, ΔH_{HB} , is not necessarily the same as that given by the enthalpy of the reaction measured in solution, $\Delta H_{\text{HB}'}$. An ideal solution is one in which the heat of mixing is 0, so the question arises as to whether -X-H and B form ideal solutions with the solvent. If the solvent is one such as benzene, which forms weak hydrogen bonds to -X-H, those bonds must be broken before the hydrogen bond to B can form. Therefore, the enthalpy measured in solution will not be the same as that which corresponds to the gas phase reaction. The same situation exists if the solvent is one that interacts with B. Mathematically, the requirement for the gas and solution phase enthalpies to be equal is that $|\Delta H_1 + \Delta H_2| = |\Delta H_3|$. If the extent to which the solvent is a participant in the process is indicated by the position of the "free" O-H stretching band, it can be seen that heptane is the most nearly "inert" solvent of those just discussed. In fact, the "inertness" decreases in the order heptane > CCl₄ > CS₂ >> C₆H₆. This series is in accord with the trend illustrated in Figure 6.10. A good test for evaluating the role (if any) of the solvent in hydrogen bonding is to determine the enthalpy of the hydrogen bond formation in different solvents to see if the measured enthalpy is the same. Although the solvent most widely used in hydrogen bonding studies has probably been CCl₄, hexane or heptane is usually a better choice.

There have been many studies on the formation of hydrogen bonds between alcohols and a wide range of bases. If the bases are of similar type (for example, all nitrogen donor atoms in amines), there is also frequently a rather good correlation between the shift of the O-H stretching band and other properties. For example, stretching frequency shifts of the OH bonds in alcohols have been correlated

with base strength of the electron pair donor. As long as the bases have similar structure, the correlations are generally satisfactory. Figure 6.11 shows such a correlation for trimethylamine and triethylamine as well as a series of methyl-substituted pyridines. It is apparent that the correlation is quite good, and it can be expressed as

$$\Delta\nu_{\text{OH}} = a \text{p}K_b + b \quad (6.26)$$

where a and b are constants. The availability of electrons on the donor atom in a base molecule determines not only its ability to bind H^+ but also its ability to attract a hydrogen atom in forming a hydrogen bond. Consequently, it is reasonable to expect some relationship to exist between base strength and hydrogen bonding ability.

Relationships between the stretching frequency shifts and hydrogen bond enthalpies have also been established. Such a correlation can be written in the form

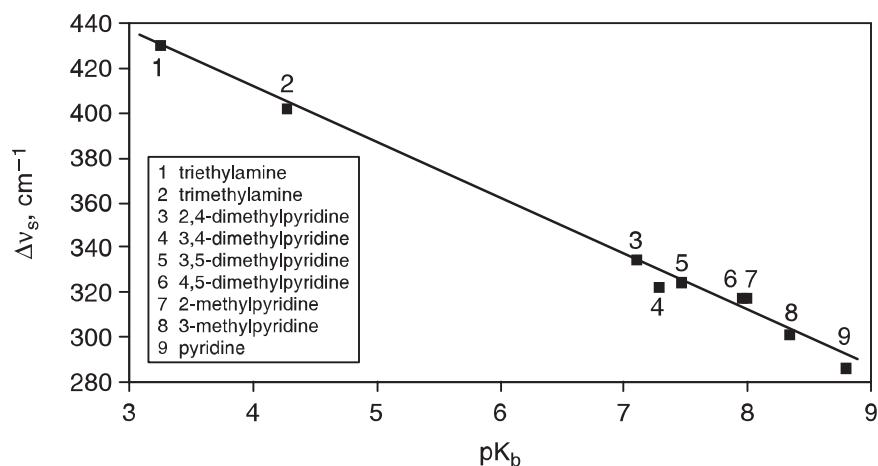
$$-\Delta H = c \Delta\nu_s + d \quad (6.27)$$

where c and d are constants. For bases of a different structural type, the constants may have different values. Many correlations of this type have been developed, and some of them are useful, empirical relationships.

Hydrogen bonding is a special type of acid-base interaction (see Chapter 9). Probably the most important equation relating hydrogen bond strengths is the equation known as the Drago four-parameter equation,

$$-\Delta H = C_A C_B + E_A E_B \quad (6.28)$$

which applies to many types of acid-base interactions. This equation is based on the assumption that a bond (including a hydrogen bond) is made up of a covalent part and an electrostatic part. The covalent contribution to the bond enthalpy is given by the product of parameters giving the covalent bonding



■ FIGURE 6.11 Shift of the OH stretching band for methanol hydrogen bonded to several bases as a function of base strength.

ability of the acid and base (C_A and C_B), and the product of the electrostatic parameters (E_A and E_B) gives the ionic contribution to the bond. When tables are available that give the needed parameters, the calculated enthalpies of interaction agree remarkably well with the experimental values. Because of the wider use of the Drago equation in other types of acid-base interactions, it will be discussed more fully in Chapter 9.

As the brief introduction to the subject presented here shows, hydrogen bonding is extremely important in all areas of chemistry. Additional topics including discussions of experimental methods for studying hydrogen bonding can be found in the references cited at the end of this chapter.

6.7 COHESION ENERGY AND SOLUBILITY PARAMETERS

Molecules have forces of attraction between them, and these intermolecular forces are responsible for many of the properties of liquids. There is a cohesion energy that holds the molecules together. The energy necessary to overcome these forces to vaporize a mole of liquid is known as the *cohesion energy* of the liquid or the *energy of vaporization*. It is related to the enthalpy of vaporization by the equation

$$\Delta H_{\text{vap}} = \Delta E_{\text{vap}} + \Delta(PV) \quad (6.29)$$

Therefore, since $\Delta(PV) = RT$

$$\Delta E_{\text{vap}} = E_c = \Delta H_{\text{vap}} - RT \quad (6.30)$$

where E_c is the cohesion energy of the liquid. The quantity E_c/V_m where V_m is the molar volume of the liquid is known as the cohesion energy density. A useful thermodynamic relationship is

$$dE = T dS - P dV \quad (6.31)$$

This equation can be written as

$$\frac{\partial E}{\partial V} = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (6.32)$$

where P is the *external* pressure. The internal pressure, P_i , is given by

$$P_i = T \left(\frac{\partial P}{\partial T} \right)_V \quad (6.33)$$

which can also be written as

$$P_i = \left(\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \right) \quad (6.34)$$

The quantity $(\partial V/\partial T)_P$ is the coefficient of thermal expansion and $(\partial V/\partial P)_T$ is the coefficient of compressibility of the liquid. For many liquids, the internal pressure is in the range 2000 to 8000 atm. Because the internal pressure is so much greater than the external pressure,

$$E_c = P_i - P \approx P_i \quad (6.35)$$

The solubility parameter, δ , is expressed in terms of the cohesion energy per unit volume by the equation

$$\delta = \sqrt{\frac{E_c}{V}} \quad (6.36)$$

where V is the molar volume. The dimensions for δ are (energy/volume)^{1/2} with suitable units being [cal/cm³]^{1/2} or cal^{1/2} cm^{-3/2}, a unit, h, known as 1 hildebrand in honor of Joel Hildebrand, who did pioneering research on the liquid state for many years. Many of the standard tables that give solubility parameters are in those units. Because 1 cal = 4.184 J, the conversion factor from cal^{1/2} cm^{-3/2} to J^{1/2} cm^{-3/2} is 4.184^{1/2} = 2.045. Both sets of units are in common use (sometimes both are indiscriminately referred to as h), and most of the extensive tables found in the older literature give values in cal^{1/2} cm^{-3/2}. The solubility parameters in J^{1/2} cm^{-3/2} for some common liquids are shown in Table 6.7.

The cohesion energies of liquids determine their mutual solubility. If two liquids have greatly differing cohesion energies, they will not mix because each liquid has a greater affinity for molecules of its own kind than for those of the other liquid. Water ($\delta = 53.2$ h) and carbon tetrachloride ($\delta = 17.6$ h) provide an example that illustrates this principle. In contrast, methanol ($\delta = 29.7$ h) and ethanol ($\delta = 26.0$ h) are completely miscible.

Solubility parameters for many liquids are available in extensive tables (see references at the end of this chapter). In order to determine solubility parameters for liquids, we need to know the heat of

Liquid	Solubility Parameter, h	Liquid	Solubility Parameter, h
C ₆ H ₁₄	14.9	CS ₂	20.5
CCl ₄	17.6	CH ₃ NO ₂	25.8
C ₆ H ₆	18.6	Br ₂	23.5
CHCl ₃	19.0	HCON(CH ₃) ^a	24.7
(CH ₃) ₂ CO	20.5	C ₂ H ₅ OH	26.0
C ₆ H ₅ NO ₂	23.7	H ₂ O	53.2
<i>n</i> -C ₅ H ₁₂	14.5	CH ₃ COOH	21.3
C ₆ H ₅ CH ₃	18.2	CH ₃ OH	29.7
XeF ₂	33.3	XeF ₄	30.9
(C ₂ H ₅) ₂ O	15.8	<i>n</i> -C ₈ H ₁₈	15.3
(C ₂ H ₅) ₃ B	15.4	(C ₂ H ₅) ₂ Zn	18.2
(CH ₃) ₃ Al ^b	20.8	(C ₂ H ₅) ₃ Al ^b	23.7
(<i>n</i> -C ₃ H ₇) ₃ Al ^b	17.0	(<i>i</i> -C ₄ H ₉) ₃ Al ^b	15.7

^a*N,N*-Dimethylformamide.
^bThese compounds are extensively dimerized.

vaporization. Over a reasonable temperature range, the relationship between the vapor pressure of a liquid and temperature is given by

$$\ln p = -\frac{\Delta H_{\text{vap}}}{RT} + C \quad (6.37)$$

where p is the vapor pressure, ΔH_{vap} is the heat of vaporization, T is the temperature (K), and C is a constant. If the vapor pressure is available at several temperatures, one way in which the heat of vaporization is determined is from the slope of the line that results when natural logarithm of the vapor pressure is plotted against $1/T$. Therefore, it is possible to evaluate the solubility parameter for a liquid if vapor pressure data are available and if the density is known so that the molar volume can be calculated.

Although Eq. (6.37) is commonly used to represent the vapor pressure as a function of temperature, it is by no means the best equation for the purpose. For many compounds, a more accurate representation of the vapor pressure is given by the Antoine equation,

$$\log p = A - \left(\frac{B}{C + t} \right) \quad (6.38)$$

In this equation, A , B , and C are constants that are different for each liquid, and t is the temperature in °C. Numerical procedures exist for determining the values for A , B , and C for a liquid if the vapor pressure is known at several temperatures. By making use of the equation

$$E_c = \Delta H_{\text{vap}} - RT \quad (6.39)$$

after determining the heat of vaporization from a plot of $\ln p$ versus $(C + t)$, the cohesion energy can be expressed as

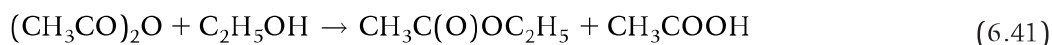
$$E_c = RT \left(\frac{2.303 BT}{(C + t)} - 1 \right) \quad (6.40)$$

This equation is the one most often used to calculate the cohesion energy of a liquid. From the molar mass and density of the liquid, the molar volume can be determined, and by means of Eq. (6.36) the value of δ can be determined. The importance of the solubility parameter for interpreting several types of interactions will now be illustrated.

The solubility parameter provides a way to assess the degree of cohesion within a liquid. The values for nonpolar liquids in which there are only relatively weak intermolecular forces are typically in the range 15 to 18 h ($\text{J}^{1/2} \text{cm}^{-3/2}$). This includes compounds such as CCl_4 , C_6H_6 , and alkanes. Molecules of these liquids interact only by London forces, so there is no strong association of molecules. For a given series of molecules (such as alkanes) it is to be expected that the value of δ should increase slightly as the molecular weight increases. This trend is observed with the solubility parameter for n -pentane being 14.5 h while that for n -octane is 15.3 h. On the other hand, molecules of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ interact by not only London forces but also dipole-dipole forces and hydrogen bonding. As a result, the solubility parameters for these compounds are in the range 25 to 30 h. It is clear that the solubility parameter can provide useful insight to the nature of the intermolecular forces in liquids.

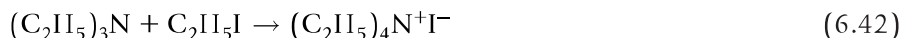
In addition to the obvious uses of solubility parameters in predicting physical properties, it is also possible in some cases to study other types of intermolecular interactions. For example, the solubility parameter for triethylboron, $(C_2H_5)_3B$, is 15.4h, whereas that for triethylaluminum $(C_2H_5)_3Al$ is 23.7h. Triethylboron is known from other studies not to associate, whereas triethylaluminum exists as dimers.

Another important use of solubility parameters is in interpreting the effects of different solvents on the rates of reactions. In a chemical reaction, it is the concentration of the transition state that determines the rate of the reaction. Depending on the characteristics of the transition state, the solvent used can either facilitate or hinder its formation. For example, a transition state that is large and has little charge separation is hindered in its formation by using a solvent that has a high value of δ . The volume of activation is usually positive for forming such a transition state which requires expansion of the solvent. A reaction of this type is the esterification of acetic anhydride with ethyl alcohol:



Because the transition state is a large aggregate with low charge separation, the rate decreases with increasing δ of the solvent. The rate of the reaction is almost 100 times as great in hexane ($\delta = 14.9$ h) as it is in nitrobenzene ($\delta = 23.7$ h).

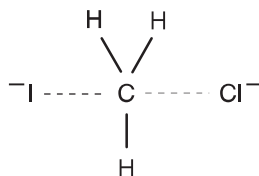
When two reacting species form a transition state in which ions are being formed, the volume of activation is often negative. The formation of such a transition state is assisted by a solvent that has a high solubility parameter. The reaction



is of this type, and it passes through a transition state in which charge is being separated. The formation of such a transition state is assisted by a solvent having a large solubility parameter. For this reaction, the rate constant increases approximately as a linear function of δ for several solvents. In the reaction



the transition state can be shown as



in which the -1 charge is spread over a large structure. Consequently, a solvent of high δ inhibits the formation of the transition state, and it is found that the rate constant for the reaction when dimethylformamide, $HCON(CH_3)_2$ ($\delta = 24.7$ h) is the solvent is over 10^6 times as great as when the solvent is CH_3OH ($\delta = 29.7$ h).

The cases just described serve to illustrate two important principles that relate the rates of reactions to the solubility parameter of the solvent. First, solvents having large δ values assist in the formation of transition states having high polarity or charge separation. Second, solvents having large δ values hinder the formation of transition states which are large, nonpolar structures. However, a large number of properties of solvents have been used to try to correlate and interpret how changing solvents alters the rates of reactions. It is clear that the solubility parameter is one important consideration when interpreting the role of the solvent in reaction kinetics or choosing a solvent as a reaction medium. It is not appropriate to discuss this topic further in a general book such as this, but the references listed should be consulted for additional details.

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