1 Solubility Parameters — An Introduction

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ABSTRACT

Solubility parameters have found their greatest use in the coatings industry to aid in the selection of solvents. They are used in other industries, however, to predict compatibility of polymers, chemical resistance, and permeation rates, and even to characterize the surfaces of pigments, fibers, and fillers. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own. The basic principle has been "like dissolves like." More recently, this has been modified to "like seeks like," as many surface characterizations have also been made, and surfaces do not (usually) dissolve. Solubility parameters help put numbers into this simple qualitative idea. This chapter describes the tools commonly used in Hansen solubility parameter (HSP) studies. These include liquids used as energy probes and computer programs to process data. The goal is to arrive at the HSP for interesting materials either by calculation or, if necessary, by experiment and preferably with agreement between the two.

INTRODUCTION

The solubility parameter has been used for many years to select solvents for coatings materials. A lack of total success has stimulated further research. The skill with which solvents can be optimally selected with respect to cost, solvency, workplace environment, external environment, evaporation rate, flash point, etc., has improved over the years as a result of a series of improvements in the solubility parameter concept and widespread use of computer techniques. Most commercial suppliers of solvents have computer programs to help with solvent selection. One can now easily predict how to dissolve a given polymer in a mixture of two solvents, neither of which can dissolve the polymer by itself.

Unfortunately, this book cannot include discussion of all the significant efforts leading to our present knowledge of the solubility parameters. An attempt is made to outline developments, provide some background for a basic understanding, and give examples of uses in practice. The key factor is to determine those affinities that the important components in a system have for each other. For many products this means evaluating or estimating the relative affinities of solvents, polymers, additives, pigment surfaces, filler surfaces, fiber surfaces, and substrates.

It is noteworthy that the concepts presented here have developed toward not just predicting solubility that requires high affinity between solvent and solute, but for predicting affinities between different polymers, leading to compatibility, and affinities to surfaces to improve dispersion and adhesion. In these applications the solubility parameter has become a tool, using well-defined liquids as energy probes, to measure the similarity, or lack of the same, of key components. Materials with widely different chemical structures may be very close in affinities. Only those materials that interact differently with different solvents can be characterized in this manner. It can be expected that many inorganic materials, such as fillers, will not interact differently with these energy probes

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as their energies are very much higher. An adsorbed layer of water on the high-energy surface can also play an important role. Regardless of these concerns, it has been possible to characterize pigments, both organic and inorganic, as well as fillers like barium sulfate, zinc oxide, etc., and also inorganic fibers (see Chapter 7). Changing the surface energies by various treatments can lead to a surface that can be characterized more readily and often interacts more strongly with given organic solvents. When the same solvents that dissolve a polymeric binder are those which interact most strongly with a surface, it can be expected that the binder and the surface have high affinity for each other.

Solubility parameters are sometimes called *cohesion energy parameters* as they are derived from the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total (cohesive) energy holding the liquid's molecules together. All types of bonds holding the liquid together are broken by evaporation, and this has led to the concepts described in more detail later. The term *cohesion energy parameter* is more appropriately used when referring to surface phenomena.

HILDEBRAND PARAMETERS AND BASIC POLYMER SOLUTION THERMODYNAMICS

The term *solubility parameter* was first used by Hildebrand and Scott.[1,2] The earlier work of Scatchard and others was contributory to this development. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (E/V)^{1/2} \tag{1.1}$$

Where V is the molar volume of the pure solvent, and *E* is its (measurable) energy of vaporization (see Equation 1.15). The numerical value of the solubility parameter in $MPa^{1/2}$ is 2.0455 times larger than that in $(cal/cm^3)^{1/2}$. The solubility parameter is an important quantity for predicting solubility relations, as can be seen from the following brief introduction.

Thermodynamics requires that the free energy of mixing must be zero or negative for the solution process to occur spontaneously. The free energy change for the solution process is given by the relation:

$$\Delta G^M = \Delta H^M - \Delta TS^M \tag{1.2}$$

where ΔG^M is the free energy of mixing, ΔH^M is the heat of mixing, T is the absolute temperature, and ΔS^M is the entropy change in the mixing process.

Equation 1.3 gives the heat of mixing as proposed by Hildebrand and Scott:

$$\Delta H^M = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 \tag{1.3}$$

The ϕ_1 and ϕ_2 are volume fractions of solvent and polymer, and V^M is the volume of the mixture. Equation 1.3 is not correct, and it has often been cited as a shortcoming of this theory in that only positive heats of mixing are allowed. It has been shown by Patterson, Delmas, and coworkers that $\Delta G^M_{noncomb}$ is given by the right-hand side of Equation 1.3 and not ΔG^M. This is discussed more in Chapter 2. The correct relation is[3–8]:

$$\Delta G^M_{noncomb} = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 \tag{1.4}$$

The noncombinatorial free energy of solution, $\Delta G^M_{noncomb}$, includes all free energy effects other than the combinatorial entropy of solution that results by simply mixing the components. Equation

1.4 is consistent with the Prigogine corresponding states theory (CST) of polymer solutions (see Chapter 2) and can be differentiated to give expressions[3,4] predicting both positive and negative heats of mixing. Therefore, both positive and negative heats of mixing can be expected from theoretical considerations and have been measured accordingly. It has been clearly shown that solubility parameters can be used to predict both positive and negative heats of mixing. Previous objections to the effect that only positive values are allowed in this theory are incorrect.

This discussion clearly demonstrates why the solubility parameter should be considered as a free energy parameter. This is more in agreement with the use of the solubility parameter plots to follow. These use solubility parameters as axes and have experimentally determined boundaries of solubility defined by the fact that the free energy of mixing is zero. The combinatorial entropy enters as a constant factor in the plots of solubility in different solvents, for example, as the concentrations are usually constant for a given study.

It is important to note that the solubility parameter, or rather the difference in solubility parameters for the solvent–solute combination, is important in determining the solubility of the system. It is clear that a match in solubility parameters leads to a zero change in noncombinatorial free energy, and the positive entropy change (the combinatorial entropy change), found on simple mixing to result in a disordered mixture compared to the pure components, will ensure that a solution is possible from a thermodynamic point of view. The maximum difference in solubility parameters that can be tolerated where the solution still occurs is found by setting the noncombinatorial free energy change equal to the combinatorial entropy change:

$$\Delta G^M_{noncomb} = T \Delta S^M_{comb} \qquad (1.5)$$

This equation clearly shows that an alternate view of the solubility situation at the limit of solubility is that it is the entropy change that dictates how closely the solubility parameters must match each other for the solution to occur.

It will be seen in Chapter 2 that solvents with smaller molecular volumes will be thermodynamically better than larger ones having identical solubility parameters. A practical aspect of this effect is that solvents with relatively low molecular volumes, such as methanol and acetone, can dissolve a polymer at larger solubility parameter differences than might be expected from comparisons with other solvents with larger molecular volumes. An average solvent molecular volume is usually taken as about 100 cc/mol. The converse is also true. Larger molecular species may not dissolve, even though solubility parameter considerations might predict they would. This can be a difficulty in predicting the behavior of plasticizers solely based on data for lower molecular weight solvents. These effects are also discussed elsewhere in this book, particularly in Chapter 2, Chapter 12, Chapter 13, and Chapter 16.

A shortcoming of the earlier solubility parameter work is that the approach was limited to regular solutions, as defined by Hildebrand and Scott,[2] and does not account for association between molecules, such as those that polar and hydrogen-bonding interactions would require. The latter problem seems to have been largely solved with the use of multicomponent solubility parameters; however, the lack of accuracy with which the solubility parameters can be assigned will always remain a problem. Using the difference between two large numbers to calculate a relatively small heat of mixing, for example, will always be problematic.

A more detailed description of the theory presented by Hildebrand, and the succession of research reports that have attempted to improve on it, can be found in Barton's extensive handbook.[9] The slightly older, excellent contribution of Gardon and Teas[10] is also a good source of related information, particularly for coatings and adhesion phenomena. The approach of Burrell,[11] who divided solvents into hydrogen bonding classes, has found numerous practical applications; the approach of Blanks and Prausnitz[12] divided the solubility parameter into two components, "non-polar" and "polar." Both are worthy of mention, however, in that the first has found wide use and the second greatly influenced the author's earlier activities. The Prausnitz article, in particular, was

farsighted in that a corresponding states procedure was introduced to calculate the dispersion energy contribution to the cohesive energy. This is discussed in more detail in Chapter 2.

It can be seen from Equation 1.2 that the entropy change is beneficial to mixing. When multiplied by the temperature, this will work in the direction of promoting a more negative free energy of mixing. This is the usual case, although there are exceptions. Increasing temperature does not always lead to improved solubility relations. Indeed, this was the basis of the pioneering work of Patterson and coworkers,[3–8] to show that subsequent increases in temperature can predictably lead to insolubility. Their work was done in essentially nonpolar systems. Increasing temperature can also lead to a nonsolvent becoming a solvent and, subsequently, a nonsolvent again with still further increase in temperature. Polymer solubility parameters do not change much with temperature, but those of a liquid frequently decrease rapidly with temperature. This situation allows a nonsolvent, with a solubility parameter that is initially too high, to pass through a soluble condition to once more become a nonsolvent as the temperature increases. These are usually "boundary" solvents on solubility parameter plots.

The entropy changes associated with polymer solutions will be smaller than those associated with liquid–liquid miscibility, for example, as the "monomers" are already bound into the configuration dictated by the polymer they make up. They are no longer free in the sense of a liquid solvent and cannot mix freely to contribute to a larger entropy change. This is one reason polymer–polymer miscibility is difficult to achieve. The free energy criterion dictates that polymer solubility parameters match extremely well for mutual compatibility, as there is little to be gained from the entropy contribution when progressively larger molecules are involved. However, polymer–polymer miscibility can be promoted by the introduction of suitable copolymers or comonomers that interact specifically within the system. Further discussion of these phenomena is beyond the scope of the present discussion; however, see Chapter 5.

HANSEN SOLUBILITY PARAMETERS

A solubility parameter approach proposed by the author for predicting polymer solubility has been in wide use. The basis of these so-called HSPs is that the total energy of vaporization of a liquid consists of several individual parts.[13–17] These arise from (atomic) dispersion forces, (molecular) permanent dipole–permanent dipole forces, and (molecular) hydrogen bonding (electron exchange). Needless to say, without the work of Hildebrand and Scott[1,2] and others not specifically referenced here, such as Scatchard, this postulate could never have been made. The total cohesive energy, E, can be measured by evaporating the liquid, i.e., breaking all the cohesive bonds. Thus the total cohesive energy is considered as being identical to the energy of vaporization. It should also be noted that these cohesive energies arise from interactions of a given solvent molecule with another of its own kind. The basis of the approach is, therefore, very simple, and it is surprising that so many different applications have been possible since 1967 when the idea was first published. A rather large number of applications are discussed in this book. Others are found in the works of Barton.[9] A lucid discussion by Barton[18] enumerates typical situations where problems occur when using solubility parameters. These appear most often where the environment causes the solvent molecules to interact, with or within themselves, differently from the way they do in situations where they make up their own environment, i.e., as pure liquids. Several cases are discussed where appropriate in the following chapters.

Materials with similar HSP have high affinity for each other. The extent of the similarity in a given situation determines the extent of the interaction. The same cannot be said of the total or Hildebrand solubility parameter.[1,2] Ethanol and nitromethane, for example, have similar total solubility parameters (26.1 vs. 25.1 MPa$^{1/2}$, respectively), but their affinities are quite different. Ethanol is water soluble, whereas nitromethane is not. Indeed, mixtures of nitroparaffins and alcohols were demonstrated in many cases to provide synergistic mixtures of two nonsolvents that dissolved

polymers.[13] This could never have been predicted by Hildebrand parameters, whereas the HSP concept readily confirms the reason for this effect.

There are three major types of interactions in common organic materials. The most general are the nonpolar interactions. These are derived from atomic forces and have also been called *dispersion interactions* in the literature. As molecules are built up from atoms, all molecules contain those types of attractive forces. For the saturated aliphatic hydrocarbons, for example, these are essentially the only cohesive interactions, and the energy of vaporization is assumed to be the same as the dispersion cohesive energy, E_D. Finding the dispersion cohesive energy as the cohesion energy of the homomorph, or hydrocarbon counterpart, is the starting point for calculating the three Hansen parameters for a given liquid. As discussed in more detail later, this is based on a corresponding states calculation.

The permanent dipole–permanent dipole interactions cause a second type of cohesion energy, *the polar cohesive energy*, E_P. These are inherently molecular interactions and are found in most molecules to one extent or another. The dipole moment is the primary parameter used to calculate these interactions. A molecule can be mainly polar in character without being water soluble, hence there is a misuse of the term *polar* in the general literature. The polar solubility parameters referred to here are well-defined, experimentally verified, and can be estimated from molecular parameters as described later. As noted previously, the most polar of the solvents include those with relatively high total solubility parameters that are not particularly water soluble, such as nitroparaffins, propylene carbonate, and tri-n-butyl phosphate. Induced dipoles have not been treated specifically in this approach but are recognized as a potentially important factor, particularly for solvents with zero dipole moments (see the Calculation of the Polar Solubility Parameter section).

The third major cohesive energy source is hydrogen bonding, E_H. This can be called more generally an *electron exchange parameter*. Hydrogen bonding is a molecular interaction and resembles the polar interactions in this respect. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds. In this perhaps oversimplified approach, the hydrogen bonding parameter has been used to more or less collect the energies from interactions not included in the other two parameters. Alcohols, glycols, carboxylic acids, and other hydrophilic materials have high-hydrogen-bonding parameters. Other researchers have divided this parameter into separate parts — for example, acid and base cohesion parameters — to allow both positive and negative heats of mixing. These approaches will not be dealt with here but are described in Barton's handbook[9] and elsewhere.[19–21] The most extensive division of the cohesive energy has been done by Karger et al.,[22] who developed a system with five parameters: dispersion, orientation, induction, proton donor, and proton acceptor. As a single parameter, the Hansen hydrogen bonding parameter has served remarkably well in the experience of the author and keeps the number of parameters to a level that allows ready practical usage.

It is clear that there are other sources of cohesion energy arising in various types of molecules from, for example, induced dipoles, metallic bonds, electrostatic interactions, or whatever type of separate energy can be defined. The author stopped with the three major types found in organic molecules. It has been recognized that additional parameters could be assigned to separate energy types. For example, the description of organometallic compounds could be an intriguing study. This would presumably parallel similar characterizations of surface-active materials, where each part of the molecule requires separate characterization for completeness. The Hansen parameters have mainly been used in connection with solubility relations, mostly, but not exclusively, in the coatings and related industries.

Solubility and swelling have been used to confirm the solubility parameter assignments of many of the liquids. Group contribution methods and suitable equations based on molecular properties were then derived from these. They make possible estimates of the three parameters for additional liquids. The goal of a prediction is to determine the similarity or difference of the cohesion energy parameters. The strength of a particular type of hydrogen bond or any other bond is important only to the extent that it influences the cohesive energy density.

HSPs do have direct applications in other scientific disciplines, such as surface science, where they have been used to characterize the wettability of various surfaces and the adsorption properties of pigment surfaces,[10,14,16,23–26] and have even led to systematic surface treatment of inorganic fibers so that they could be readily incorporated into polymers of low-solubility parameters such as polypropylene[27] (see also Chapter 7). Many widely different applications have been discussed by Barton[9] and Gardon.[28] Surface characterizations have not been given the attention deserved in terms of a unified similarity-of-energy approach. The author can certify that thinking in terms of similarity of energy, whether surface or cohesive energies, can lead to rapid decisions and plans of action in critical situations that lack data. In other words, the everyday industrial crisis situation often can be reduced in scope by appropriate systematic approaches based on similarity of energy. The success of the HSPs for surface applications are not surprising in view of the similarity of predictions offered by these, and the Prigogine corresponding states theory of polymer solutions discussed in Chapter 2. Flory also emphasized that it is the surface of molecules that interact to produce solutions,[29] so the interactions of molecules residing in surfaces should clearly be included in any general approach to interactions among molecules. Surface mobility and surface rotation are important factors in environmental stress cracking (Chapter 14), certain biological phenomena (Chapter 15), the wetting of surfaces, and in other important phenomena relating to nanotechnology (Chapter 18).

The basic equation governing the assignment of Hansen parameters is that the total cohesion energy, E, must be the sum of the individual energies that make it up.

$$E = E_D + E_P + E_H \qquad (1.6)$$

Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen D, P, and H components.

$$E/V = E_D/V + E_P/V + E_H/V \qquad (1.7)$$

$$\delta^2 = \delta^2_D + \delta^2_P + \delta^2_H \qquad (1.8)$$

To sum up this section, it is emphasized that HSPs quantitatively account for the cohesion energy (density). Up to this point of time, an experimental latent heat of vaporization has been considered a more reliable method to arrive at a cohesion energy rather than using molecular orbital calculations or other calculations based on potential functions. Indeed, the goal of such extensive calculations for polar and hydrogen bonding molecules should be to accurately arrive at the energy of vaporization. The statistical thermodynamics approach of Panayiotou and coworkers reported in Chapter 3 may have changed this. An alternative method of calculating the three parameters has been presented, but full evaluation of this new information has not been possible as yet.

METHODS AND PROBLEMS IN THE DETERMINATION OF PARTIAL SOLUBILITY PARAMETERS

The best method to calculate individual HSPs depends to a great extent on what data are available. The author originally adopted an essentially experimental procedure and established values for 90 liquids based on solubility data for 32 polymers.[13] This procedure involved calculation of the nonpolar parameter according to the procedure outlined by Blanks and Prausnitz.[12] This calculation procedure is still in use and is considered the most reliable and consistent one for this parameter. It is outlined in the following section. The division of the remaining cohesive energy between the polar and hydrogen bonding interactions was initially done by trial and error to fit experimental polymer solubility data. A key to parameter assignments in this initial trial-and-error approach was

that mixtures of two nonsolvents could be systematically and synergistically (but predictably) found to dissolve given polymers. This meant that these had parameters placing them on opposite sides of the solubility region, a spheroid. Using a large number of such predictably synergistic systems as a basis, reasonably accurate divisions into the three energy types were possible.

Using the experimentally established, approximate, δ_P and δ_H parameters, Hansen and Skaarup[15] found that the Böttcher equation (Equation 10.25) could be used to calculate the polar parameter quite well, and this led to a revision of the earlier values to those now accepted for the same liquids. These values were also consistent with the experimental solubility data for 32 polymers available at that time and with Equation 1.6. Furthermore, Skaarup developed the equation for the solubility parameter "distance," Ra, between two materials based on their respective partial solubility parameter components:

$$(Ra)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \qquad (1.9)$$

This equation was developed from plots of experimental data where the constant "4" was found convenient and correctly represented the solubility data as a sphere encompassing the good solvents (see Chapter 5). When the scale for the dispersion parameter is doubled, in comparison with the other two parameters essentially spherical, rather than spheroidal, regions of solubility are found. This greatly aids two-dimensional plotting and visualization. There are, of course, boundary regions where deviations can occur. These are most frequently found to involve the larger molecular species as being less effective solvents compared to their smaller counterparts that define the solubility sphere. Likewise, smaller molecular species such as acetone, methanol, nitromethane, and others often appear as outliers, in that they dissolve a polymer even though they have solubility parameters placing them at a distance greater than the experimentally-determined radius of the solubility sphere, Ro. This dependence on molar volume is inherent in the theory developed by Hildebrand, Scott, and Scatchard discussed previously. Smaller molar volume favors lower ΔG^M, as discussed in Chapter 2. This in turn promotes solubility. Such smaller-molecular-volume species that dissolve "better" than predicted by comparisons, based on solubility parameters alone, should not necessarily be considered outliers.

The molar volume is frequently and successfully used as a fourth parameter to describe the effects of molecular size. For example, these are especially important in correlating diffusional phenomena with HSP (see Chapter 12, Chapter 13, and Chapter 16). The author has preferred to retain the three, well-defined partial-solubility parameters with a fourth, separate, molar volume parameter, rather than multiplying the solubility parameters by the molar volume raised to some power to redefine them.

The reason for the experimentally determined constant 4 in Equation 1.9 will be discussed in more detail in Chapter 2. It will be noted here, however, that the constant 4 is theoretically predicted by the Prigogine corresponding states theory of polymer solutions when the geometric mean is used to estimate the interaction in mixtures of dissimilar molecules.[30] The constant 4 differentiates between atomic and molecular intereactions. This is exceptionally strong evidence that dispersion, permanent dipole–permanent dipole, and hydrogen bonding interactions all follow the geometric mean rule. Patterson and coworkers have been especially instrumental in relating the Prigogine theory to solubility parameters and to the Flory–Huggins theory of polymer solutions.[3–8] The HSP approach of dividing the cohesive energy into parts derived from different types of cohesive forces has been confirmed both by experimental studies, as well as the Prigogine theory. The use of the geometric mean is basic to this agreement between the HSP approach and that of Prigogine (see Chapter 2).

The approach of optimizing solubility data to spheres is still very much in use. Plotting regions of solubility based on experimental solubility data, or computer-optimizing boundaries of solubility by locating the maximum difference in solubility parameters allowed by Equation 1.9 are both used. The total free energy of mixing, ΔG^M, is equal to zero on the boundary. It should be recognized

that using the solubility parameters relating to $\Delta G^M_{noncomb}$ in Equation 1.4 differs from this by the combinatorial entropy of mixing.

Another promising approach to arrive at the HSP for materials based on experimental data is to use multivariable analysis of one type or another, as discussed in Chapter 5. This type of approach has not been attempted by the author, but it clearly has advantages in some cases. The author's preferred approach of locating the polymer HSP as the center of a sphere has a problem in that it is, in reality, the poor solvents or nonsolvents located near the boundary of the sphere that fix the boundary (and center) rather than the best solvents in the middle. This may present problems for smaller sets of data, but it is an advantage when extrapolating into regions of HSP higher than those of any liquid that can be used in testing. This is discussed in more detail in Chapter 5 and the definition of the limited segment of the boundary of the HSP sphere derivable from such correlations is based on Equation 1.9.

Equation 1.9 is readily used on a computer (or on a hand calculator), and supplementary relations allow easier scanning of large sets for data. It is obvious that solubility, or high affinity, requires that Ra be less than Ro. The ratio Ra/Ro has been called the *RED number*, reflecting the relative energy difference.

$$RED = Ra/Ro \qquad (1.10)$$

A RED number of 0 is found for no energy difference, RED numbers less than 1.0 indicate high affinity; RED equal to or close to 1.0 is a boundary condition; and progressively higher RED numbers indicate progressively lower affinities. Scanning a computer output for RED numbers less than 1.0, for example, rapidly allows location of the most interesting liquids for a given application.

Parenthetically, it should be noted that the ratio of Ra to Ro is really a ratio of quantities having the same units as the solubility parameter. The ratio $(Ra/Ro)^2 = (RED)^2$ is a ratio of cohesion energies. The latter quantity is important for relating the HSP approach to that of Huggins and Flory, as discussed in Chapter 2.

The revised set of parameters for the 90 original solvents was the basis for group contribution procedures developed (most notably) by van Krevelen,[31] Beerbower,[32] and Hansen and Beerbower,[17] who also used Fedors' work.[33] These various developments have been summarized by Barton,[9] although Beerbower's latest values have only appeared in the National Aeronautics and Space Administration (NASA) document.[32] Table 1.1 is an expanded table of Beerbower group contributions, which was distributed among those who were in contact with Beerbower in the late 1970s. The majority of the data in this table, as well as Table 1.2, have also appeared in Reference 34. Beerbower also developed a simple equation for the polar parameter,[17] which involved only the dipole moment and the square root of the molar volume. This is also given later (Equation 1.13) and has been found quite reliable by Koenhen and Smolders.[35] This equation has been found reliable by the author as well, giving results generally consistent with Equation 1.6 to Equation 1.8, which, again, is the basis of the whole approach. Koenhen and Smolders also give correlation coefficients for other calculation procedures to arrive at the individual Hansen parameters.

The group contributions in Table 1.1 have been used extensively to arrive at the collection of HSP data in Appendix Table A.1. Most of the chemicals of primary interest for which full data are available are presumably already in this table. The trend has been to calculate HSP for larger and still larger molecules. Many of these have multiple groups, and it becomes more and more difficult to make decisions as to how to treat them best. At times the HSP for the larger molecules can be estimated from the HSP of larger segments that make them up. Rather than expanding Table 1.1 with additional data, except as noted briefly later, the usual practice has been to locate chemicals with similar groups and to use their HSP values in a group contribution-type calculation.

The procedure has developed to the point where its principle features can be identified in the following table. If a boiling point is available, the procedures for calculating δ_D have been used. If a boiling point is not available, the similarity with related molecules has been used. If a dipole

moment is available, the procedures given here were used in preference to group contributions. If necessary, group contributions can be derived from similar molecules to the one in question, when dipole moments are available for these, and not for the molecule in question. There is often a change in the group contribution as a function of molecular size. This is the main reason for the lack of expansion of Table 1.1. It is thought best that the uncertainty be clear to the user. For example, it has been found that the group contribution for the polar component of aliphatic esters should not be less than 300 cal/mol as given in Table 1.1. This is necessary to prevent δ_P for materials like plasticizers from being clearly too low, based on their compatibility with, for example, polyvinyl chloride. Sulfur containing compounds have also been somewhat difficult in this respect, with major changes in estimated group contributions depending on molecular weight of the chemical in question. Group contributions for sulfur, amides, and other groups not found in Table 1.1 can be easily derived from the data on similar compounds reported in Appendix Table A.1. The same is true of the δ_H component. The problem with this procedure is obvious: any error or distortion of value for a class of compounds is perpetuated. This has been recognized and dealt with to the extent possible, but there are limits to what can be done with limited data. The scope of this situation has been beyond the resources available for its fully satisfactory resolution. The extensive list of group contributions at the end of Chapter 3 provides what may be a partial replacement and/or a supplement for Table 1.1. This requires some experience with the techniques involved.

A sizable number of materials have been assigned HSPs using the procedures described here. Many of these have not been published. Exxon Chemical Corporation[36,37] has indicated a computer program with data for over 500 solvents and plasticizers, 450 resins and polymers, and 500 pesticides. The author's files contain the three parameters for about 1200 chemicals (See Appendix Table A.1), although several of them appear with two sets of possible values awaiting experimental confirmation. In some cases, this is due to questionable physical data, for example, for latent heats of vaporization, or wide variations in reported dipole moments. Another reason is that some liquids are chameleonic,[38] as defined by Hoy, in that they adopt configurations depending on their environment. Hoy[38] cites the formation of cyclic structures for glycol ethers with (nominally) linear structure. The formation of hydrogen-bonded tetramers of alcohols in a fluoropolymer has also been pointed out.[39] The term *compound formation* can be found in the older literature, particularly where mixtures with water were involved and structured species were postulated to explain phenomena based on specific interactions among the components of the mixtures. Barton has discussed some of the situations where cohesion parameters need a more careful use, and points out that Hildebrand or Hansen parameters must be used with particular caution where the extent of donor–acceptor interactions, especially, hydrogen bonding within a compound, is very different from that between compounds.[18] Amines, for example, are known to associate with each other. Pure component data cannot be expected to predict the behavior in such cases.

Still another reason for difficulties is the large variation of dipole moments reported for the same liquid. The dipole moment for some liquids depends on their environment, as discussed later. A given solvent can be listed with different values in files to keep these phenomena in mind.

Large data sources greatly enhance a search for similar materials and the locating of new solvents, as an example, for a polymer for which there are limited data. Unfortunately, different authors have used different group contribution techniques, and there is a proliferation of different "Hansen" parameters for the same chemicals in the literature. This would seem to be an unfortunate situation, but may ultimately provide benefits. In particular, partial solubility parameter values found in Hoy's extensive tables[9,40] are not compatible with the customary Hansen parameters reported here. Hoy has provided an excellent source of total solubility parameters. He independently arrived at the same type of division of cohesion energies as Hansen, although the methods of calculation were quite different.

Many solvent suppliers have also presented tables of solvent properties and/or use computer techniques with these tables in their technical service. Partial solubility parameters not taken directly from earlier well-documented sources should be used with caution. The Hoy dispersion parameter,

TABLE 1.1
Group Contributions to Partial Solubility Parameters

Functional Group	Molar Volume,[a] ΔV (cm³/mol)		London Parameter, $\Delta V\delta_D^2$ (cal/mol)			Polar Parameter, $\Delta V\delta_P^2$ (cal/mol)			Electronic Transfer Parameter, $\Delta V\delta_H^2$ (cal/mol)		Total Parameter[a] $\Delta V\delta^2$ (cal/mol)	
	Aliphatic	Aromatic	Alkane	Cyclo	Aromatic	Alkane	Cyclo	Aromatic	Aliphatic	Aromatic	Aliphatic	Aromatic
CH_3	33.5	Same	1,125	Same	Same	0	0	0	0	0	1,125	Same
$CH_2<$	16.1	Same	1,180	Same	Same	0	0	0	0	0	1,180	Same
$-CH<$	−1.0	Same	820	Same	Same	0	0	0	0	0	820	Same
$>C<$	−19.2	Same	350	Same	Same	0	0	0	0	0	350	Same
CH_2 = olefin	28.5	Same	850 ± 100	?	?	25 ± 10	?	?	180 ± 75	?	1,030	Same
$-CH$ = olefin	13.5	Same	875 ± 100	?	?	18 ± 5	?	?	180 ± 75	?	1,030	Same
$>C$ = olefin	−5.5	Same	800 ± 100	?	?	60 ± 10	?	?	180 ± 75	?	1,030	Same
Phenyl-	—	71.4	—	—	7,530	—	—	50 ± 25	—	50 ± 50[c]	—	7630
C-5 ring (saturated)	16	—	—	250	—	0	0	—	0	—	250	—
C-6 ring	16	Same	—	250	250	0	0	0	0	0	250	250
−F	18.0	22.0	0	0	0	1,000 ± 150	?	700 ± 100	0	0	1,000	800[b]
=F_2 twin[f]	40.0	48.0	0	0	0	700 ± 250[c]	?	500 ± 250[c]	0	0	1,700	1,360[b]
≡F_3 triplet[f]	66.0	78.0	0	0	0	?	?	?	0	0	1,650	1,315[b]
−Cl	24.0	28.0	1,400 ± 100	?	1,300 ± 100	1,250 ± 100	1,450 ± 100	800 ± 100	100 ± 20[c]	Same	2,760	2,200[b]
=Cl_2 twin[f]	52.0	60.0	3,650 ± 160	?	3,100 ± 175[c]	800 ± 150	?	400 ± 150[c]	165 ± 10[c]	180 ± 10[c]	4,600	3,670[b]
≡Cl_3 triplet[f]	81.9	73.9	4,750 ± 300[c]	?	?	300 ± 100	?	?	350 ± 250[c]	?	5,400	4,300[b]
−Br	30.0	34.0	1,950 ± 300[c]	1,500 ± 175	1,650 ± 140	1,250 ± 100	1,700 ± 150	800 ± 100	500 ± 100	500 ± 100	3,700	2,960[b]
=Br_2 twin[f]	62.0	70.0	4,300 ± 300[c]	?	3,500 ± 300[c]	800 ± 250[c]	?	400 ± 150[c]	825 ± 200[c]	800 ± 250[c]	5,900	4,700[b]
≡Br_3 triplet[f]	97.2	109.2	5,800 ± 400[c]	?	?	350 ± 150[c]	?	?	1,500 ± 300[c]	?	7,650	6,100[b]
−I	31.5	35.5	2,350 ± 250[c]	2,200 ± 250[c]	2,000 ± 250[c]	1,250 ± 100	1,350 ± 100	575 ± 100	1,000 ± 200[c]	1,000 ± 200[c]	4,550	3,600[b]
I_2 twin[e]	66.6	74.6	5,500 ± 300[c]	?	4,200 ± 300[c]	800 ± 250[c]	?	400 ± 150[c]	1,650 ± 250[c]	1,800 ± 250[c]	8,000	6,400[b]
≡I_3 triplet[e]	111.0	123.0	?	?	?	?	?	?	?	?	11,700	9,350[b]
−O− ether	3.8	Same	0	0	0	500 ± 150	600 ± 150	450 ± 150	450 ± 25	1,200 ± 100	800	(1,650 ± 150)
>CO ketone	10.8	Same	—[e]	2,350 ± 400	2,800 ± 325	(15, 000 ± 7%)/V	1,000 ± 300	950 ± 300	800 ± 250[d]	400 ± 125[c]	4,150	Same
−CHO	(23.2)	(31.4)	950 ± 300	?	550 ± 275	2,100 ± 200	3,000 ± 500	2,750 ± 200	1,000 ± 200	750 ± 150	(4,050)	Same
−COO-ester	18.0	Same	—[f]	?	—[f]	(56,000 ± 12%)/V	?	(338,000 ± 10%)/V	1,250 ± 150	475 ± 100[c]	4,300	Same
−COOH	28.5	Same	3,350 ± 300	3,550 ± 250	3,600 ± 400	500 ± 150	300 ± 50	750 ± 350	2,750 ± 250	2,250 ± 250[c]	6,600	Same
−OH	10.0	Same	1,770 ± 450	1,370 ± 500	1,870 ± 600	700 ± 200	1,100 ± 300	800 ± 150	4,650 ± 400	4,650 ± 500	7,120	Same

=(OH)$_2$ twin or adjacent	26.0	Same	0	?	?	1,500 ± 100	?	?	9,000 ± 600	9,300 ± 600	10,440	Same
–CN	24.0	Same	1,600 ± 850[c]	?	0	4,000 ± 800[c]	?	3,750 ± 300c	500 ± 200[d]	400 ± 125[c]	4,150	Same
–NO$_2$	24.0	32.0	3,000 ± 600	?	2,550 ± 125	3,600 ± 600	?	1,750 ± 100	400 ± 50[d]	350 ± 50[c]	7,000	(4,400)
–NH$_2$ amine	19.2	Same	1,050 ± 300	1,050 ± 450[c]	150 ± 150[c]	600 ± 200	600 ± 350[c]	800 ± 200	1,350 ± 200	2,250 ± 200[d]	3,000	Same
>NH$_2$ amine	4.5	Same	1,150 ± 225	?	?	100 ± 50	?	?	750 ± 200	?	2,000	Same
–NH$_2$ amide	(6.7)	Same	?	?	?	?	?	?	2,700 ± 550[c]	?	(5,850)	Same
≡PO$_4$ ester	28.0	Same	—[e]	?	?	(81,000 ± 10%)/V	?	?	3,000 ± 500	?	(7,000)	Same

[a] Data from Fedors, R.F., A method for estimating both the solubility parameters and molar volumes of liquids, *Polym. Eng. Sci.*, 14(2), 147–154, 472, 1974. With permission.

[b] These values apply to halogens attached directly to the ring and also to halogens attached to aliphatic double-bonded C atoms.

[c] Based on very limited data. Limits shown are roughly 95% confidence; in many cases, values are for information only and not to be used for computation.

[d] Includes unpublished infrared data.

[e] Use formula in $\Delta V \delta_P^2$ column to calculate, with V for total compound.

[f] Twin and triplet values apply to halogens on the same C atom, except that $\Delta V \delta_P^2$ also includes those on adjacent C atoms.

Source: From Hansen, C. M., *Paint Testing Manual*, Manual 17, Koleske, J. V., Ed., American Society for Testing and Materials, Philadelphia, 1995, 388. Copyright ASTM. Reprinted with permission.

TABLE 1.2
Lydersen Group Constants

Group	Aliphatic, ΔT	Cyclic, ΔT	Δ_T^P	Aliphatic, ΔP	Cyclic, ΔP
CH_3	0.020	—	0.0226	0.227	—
CH_2	0.020	0.013	0.0200	0.227	0.184
>CH–	0.012	0.012	0.0131	0.210	0.192
>C<	0.000	–0.007	0.0040	0.210	0.154
CH_2	0.018	—	0.0192	0.198	—
CH–	0.018	0.011	0.0184	0.198	0.154
C<	0.000	0.011	0.0129	0.198	0.154
CH aromatic	—	—	0.0178	—	—
CH aromatic	—	—	0.0149	—	—
–O–	0.021	0.014	0.0175	0.16	0.12
>O epoxide	—	—	0.0267	—	—
–COO–	0.047	—	0.0497	0.47	—
>C=O	0.040	0.033	0.0400	0.29	0.02
–CHO	0.048	—	0.0445	0.33	—
$–CO_2O$	—	—	0.0863	—	—
–OH→	—	—	0.0343	0.06	—
–H→	—	—	–0.0077	—	—
–OH primary	0.082	—	0.0493	—	—
–OH secondary	—	—	0.0440	—	—
–OH tertiary	—	—	0.0593	—	—
–OH phenolic	0.035	—	0.0060	–0.02	
$–NH_2$	0.031	—	0.0345	0.095	—
–NH–	0.031	0.024	0.0274	0.135	0.09
>N–	0.014	0.007	0.0093	0.17	0.13
–C≡N	0.060	—	0.0539	0.36	—
–NCO	—	—	0.0539	—	—
HCON<	—	—	0.0546	—	—
–CONH–	—	—	0.0843	—	—
–CON<	—	—	0.0729	—	—
$–CONH_2$	—	—	0.0897	—	—
–OCONH–	—	—	0.0938	—	—
–S–	0.015	0.008	0.0318	0.27	0.24
–SH	0.015	—	—	—	—
–Cl 1°	0.017	—	0.0311	0.320	—
–Cl 2°	—	—	0.0317	—	—
Cl_1 twin	—	—	0.0521	—	—
Cl aromatic	—	—	0.0245	—	—
–Br	0.010	—	0.0392	0.50	—
–Br aromatic	—	—	0.0313	—	—
–F	0.018	—	0.006	0.224	—
–I	0.012	—	—	0.83	—

TABLE 1.2 (CONTINUED)
Lydersen Group Constants

Group	Aliphatic, ΔT	Cyclic, ΔT	Δ_T^P	Aliphatic, ΔP	Cyclic, ΔP
Conjugation	—	—	0.0035	—	—
cis double bond	—	—	–0.0010	—	—
trans double bond	—	—	–0.0020	—	—
4 Member ring	—	—	0.0118	—	—
5 Member ring	—	—	0.003	—	—
6 Member ring	—	—	–0.0035	—	—
7 Member ring	—	—	0.0069	—	—
Ortho	—	—	0.0015	—	—
Meta	—	—	0.0010	—	—
Para	—	—	0.0060	—	—
Bicycloheptyl	—	—	0.0034	—	—
Tricyclodecane	—	—	0.0095	—	—

Source: Hansen, C.M., Solubility parameters, in *Paint Testing Manual*, Manual 17, Koleske, J.V., Ed., American Society for Testing and Materials, Philadelphia, PA, 1995, 383–404. Reprinted with permission.

in particular, is consistently lower than that found by Hansen. Hoy subtracts estimated values of the polar and hydrogen-bonding energies from the total energy to find the dispersion energy. This allows for more calculational error and underestimates the dispersion energy, as the Hoy procedure does not appear to fully separate the polar and hydrogen-bonding energies. The van Krevelen dispersion parameters appear to be too low. The author has not attempted these calculations, being completely dedicated to the full procedure based on corresponding states described here, but values estimated independently using the van Krevelen dispersion parameters are clearly low. A comparison with related compounds or the similarity principle gives better results than those found from the van Krevelen dispersion group contributions.

In the following, calculation procedures and experience are presented according to the procedures most reliable for the experimental and/or physical data available for a given liquid.

CALCULATION OF THE DISPERSION SOLUBILITY PARAMETER δ_D

The δ_D parameter is calculated according to the procedures outlined by Blanks and Prausnitz.[12] Figure 1.1 to Figure 1.3 can be used to find this parameter, depending on whether the molecule of interest is aliphatic, cycloaliphatic, or aromatic. These figures have been inspired by Barton,[9] who converted earlier data to Standard International (SI) units. All three of these figures have been straight-line extrapolated into a higher range of molar volumes than that reported by Barton. Energies found with these extrapolations have also provided consistent results. As noted earlier, the solubility parameters in SI units (MPa$^{1/2}$) are 2.0455 times larger than (ca1/cc)$^{1/2}$ in the older cgs centimeter gram second (cgs) system, which still finds extensive use in the U.S., for example.

The figure for the aliphatic liquids gives the dispersion cohesive energy, E_D, whereas the other two figures directly report the dispersion cohesive energy density, c. The latter is much simpler to use, as one need only take the square root of the value found from the figure to find the respective partial solubility parameter. Barton also presented a similar figure for the aliphatic solvents, but it
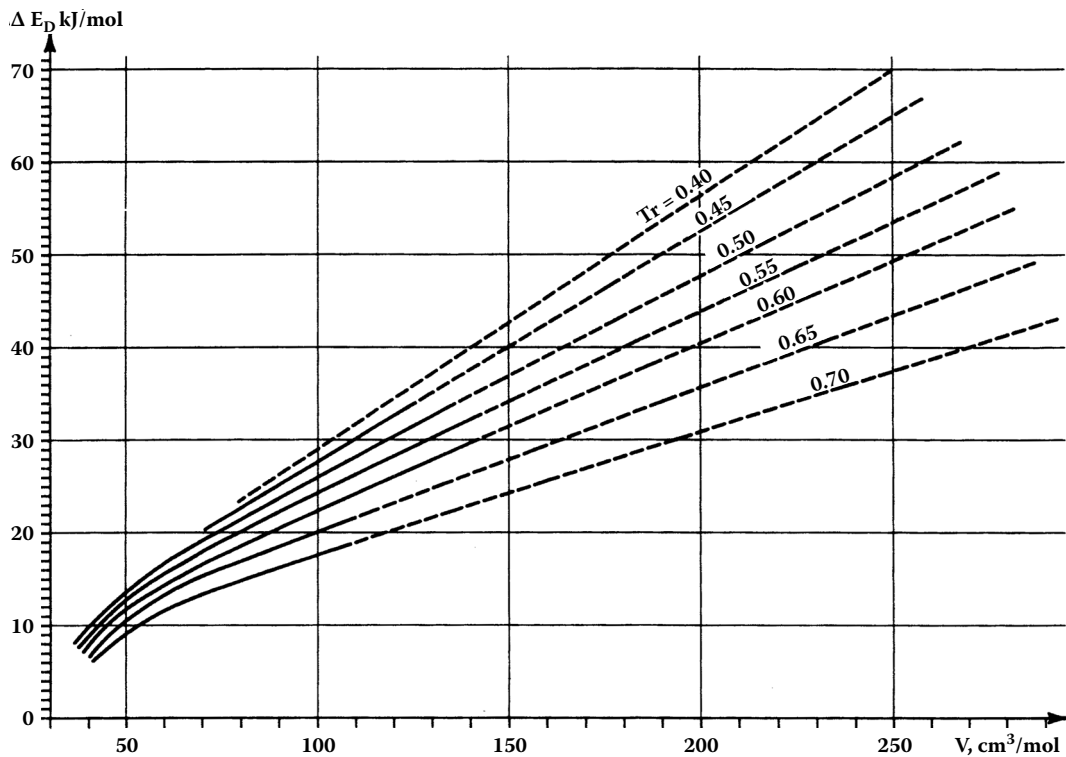
FIGURE 1.1 Energy of vaporization for straight chain hydrocarbons as a function of molar volume and reduced temperature. (From Hansen, C. M., *Paint Testing Manual*, Manual 17, Koleske, J. V., Ed., American Society for Testing and Materials, Philadelphia, 1995, 389. Copyright ASTM. Reprinted with permission.)

FIGURE 1.2 Cohesive energy density for cycloalkanes as a function of molar volume and reduced temperature. (From Hansen, C. M., *Paint Testing Manual*, Manual 17, Koleske, J. V., Ed., American Society for Testing and Materials, Philadelphia, 1995, 389. Copyright ASTM. Reprinted with permission.)
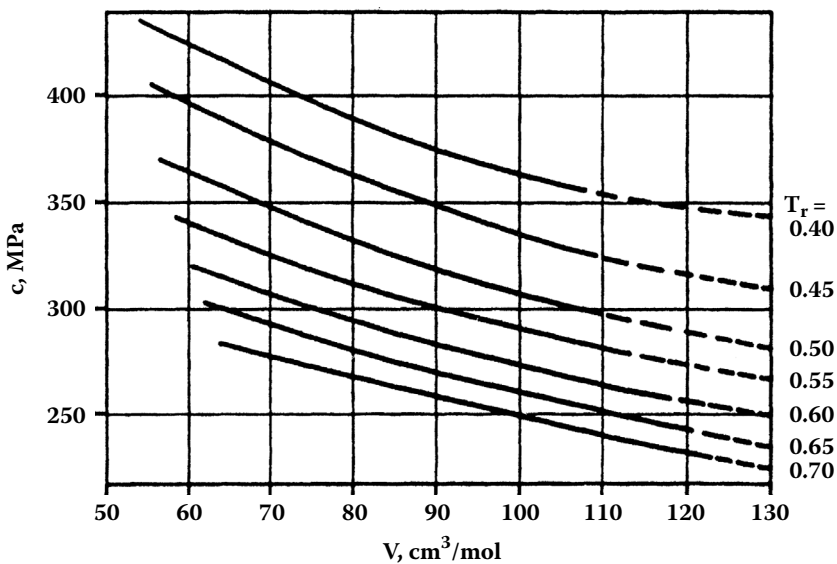
FIGURE 1.3 Cohesive energy density for aromatic hydrocarbons as a function of molar volume and reduced temperature. (From Hansen, C. M., *Paint Testing Manual*, Manual 17, Koleske, J. V., Ed., American Society for Testing and Materials, Philadelphia, 1995, 389. Copyright ASTM. Reprinted with permission.)
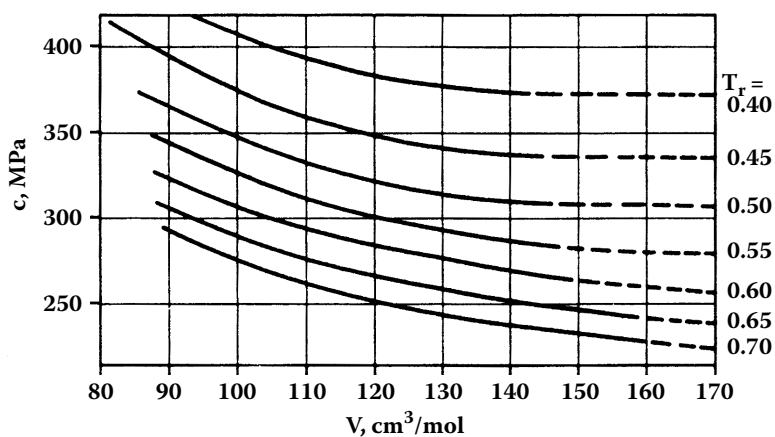
is inconsistent with the energy figure and in error. Its use is not recommended. When substituted cycloaliphatics or substituted aromatics are considered, simultaneous consideration of the two separate parts of the molecule is required. The dispersion energies are evaluated for each of the molecules involved, and a weighted average is taken for the molecule of interest based on the number of significant atoms. For example, hexyl benzene would be the arithmetic average of the dispersion energies for an aliphatic and an aromatic liquid, each with the given molar volume of hexyl benzene. Liquids such as chlorobenzene, toluene, and ring compounds with alkyl substitutions that have only two or three carbon atoms have been considered only as cyclic compounds. Such weighting has been found necessary to satisfy Equation 1.6.

The critical temperature, T_c, is required to use the dispersion energy figures. If the critical temperature cannot be found, it must be estimated. A table of the Lydersen group contributions,[41] ΔT, as given by Hoy[40] for calculation of the critical temperature is included as Table 1.2. In some cases, the desired groups may not be in the table, which requires some educated guessing. The end result does not appear too sensitive to these situations. The normal boiling temperature, T_b, is also required in this calculation. This is not always available and must be estimated by similarity, group contribution, or some other technique. The Lydersen group contribution method involves the use of Equation 1.11 and Equation 1.12 as follows:

$$T_b/T_c = 0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2 \tag{1.11}$$

and

$$T_r = T/T_c \tag{1.12}$$

where T has been taken as 298.15 K.

The dispersion parameter is based on atomic forces. The size of the atom is important. It has been found that corrections are required for atoms significantly larger than carbon, such as chlorine, sulfur, bromine, etc., but not for oxygen or nitrogen that have a similar size. The carbon atom in hydrocarbons is the basis of the dispersion parameter in its present form. These corrections are applied by first finding the dispersion cohesive energy from the appropriate figure. This requires multiplication by the molar volume for the cyclic compounds using data from the figures here, as these figures give the cohesive energy densities. The dispersion cohesive energy is then increased by adding on the correction factor. This correction factor for chlorine, bromine, and sulfur has been

taken as 1650 J/mol for each of these atoms in the molecule. Dividing by the molar volume and then taking the square root gives the (large atom corrected) dispersion solubility parameter.

The need for these corrections has been confirmed many times, both for interpretation of experimental data and to allow Equation 1.6 to Equation 1.8 to balance. Research is definitely needed in this area. The impact of these corrections is, of course, larger for the smaller molecular species. Taking square roots of the larger numbers involved with the larger molecular species reduces the errors involved in these cases, as the corrections are relatively small.

It can be seen from the dispersion parameters of the cyclic compounds that the ring has an effect similar to increasing the effective size of the interacting species. The dispersion energies for cycloaliphatic compounds are larger than their aliphatic counterparts, and they are higher for aromatic compounds than their corresponding cycloaliphatics. Similar effects also appear with the ester group. This group appears to act as if it were, in effect, an entity that is larger than the corresponding compound containing only carbon (i.e., its homomorph), and it has a higher dispersion solubility parameter without any special need for corrections.

The careful evaluation of the dispersion cohesive energy may not have a major impact on the value of the dispersion solubility parameter, because square roots of rather large numbers are taken. Larger problems arise because of Equation 1.6. Energy assigned to the dispersion portion cannot be reused when finding the other partial parameters using Equation 1.6 (or Equation 1.8). This is one reason group contributions are recommended in some cases, as discussed later.

CALCULATION OF THE POLAR SOLUBILITY PARAMETER δ_P

The earliest assignments of a "polar" solubility parameter were given by Blanks and Prausnitz.[12] These parameters were, in fact, the combined polar and hydrogen bonding parameters as used by Hansen, and they cannot be considered polar in the current context. The first Hansen polar parameters[13] were reassigned new values by Hansen and Skaarup according to the Böttcher equation (Equation 10.25).[15] This equation requires the molar volume, the dipole moment (DM), the refractive index, and the dielectric constant. These are not available for many compounds, and the calculation used is more difficult than the much simpler equation developed by Hansen and Beerbower[17]:

$$\delta_P = 37.4(DM)/V^{1/2} \tag{1.13}$$

The constant 37.4 gives this parameter in SI units.

Equation 1.13 has been consistently used by the author over the past years, particularly in view of its reported reliability.[35] This reported reliability appears to be correct. The molar volume must be known or estimated in one way or another. This leaves only the dipole moment to be found or estimated. Standard reference works have tables of dipole moments, with the most extensive listing still being McClellan.[42] Other data sources also have the same, as well as other relevant parameters, and data such as latent heats and critical temperatures. The Design Institute for Physical Property Research (DIPPR)[43] database has been found useful for many compounds of reasonably common usage, but many interesting compounds are not included in the DIPPR. When no dipole moment is available, similarity with other compounds, group contributions, or experimental data can be used to estimate the polar solubility parameter.

It must be noted that the fact of zero dipole moment in symmetrical molecules is not basis enough to assign a zero polar solubility parameter. An outstanding example of variations of this kind can be found with carbon disulfide. The reported dipole moments are mostly 0 for gas phase measurements, supplemented by 0.08 in hexane, 0.4 in carbon tetrachloride, 0.49 in chlorobenzene, and 1.21 in nitrobenzene. There is a clear increase with increasing solubility parameter of the media. The latter and the highest value has been found experimentally most fitting for correlating permeation through a fluoropolymer film used for chemical protective clothing.[44] Many fluoropolymers

have considerable polarity. The lower dipole moments seem to fit in other instances. Diethyl ether has also presented problems as an outlier in terms of dissolving or not and permeating rapidly or not. Here, the reported dipole moments[42] vary from 0.74 to 2.0, with a preferred value of 1.17 and 1.79 in chloroform. Choosing a given value seems rather arbitrary. The chameleonic cyclic forms of the linear glycol ethers would also seem to provide a basis for altered dipole moments in various media.[38]

When Equation 1.13 cannot be used, the polar solubility parameter has been found using the Beerbower table of group contributions, by similarity to related compounds and/or by subtraction of the dispersion and hydrogen bonding cohesive energies from the total cohesive energy. The question in each case is, "Which data are available and judged most reliable?" New group contributions can also be developed from related compounds whose dipole moments are available. These new polar group contributions then become supplementary to the Beerbower table.

For large molecules, especially those with long hydrocarbon chains, the accurate calculation of the relatively small polar (and hydrogen bonding) contributions present special difficulties. The latent heats are not generally available with sufficient accuracy to allow subtraction of two large numbers from each other to find a very small one. In such cases, the similarity and group contribution methods are thought best. Unfortunately, latent heats found in a widely used handbook[45] are not clearly reported as to the reference temperature. There is an indication that these are 25°C data, but checking indicated many of the data to be identical with boiling point data reported elsewhere in the literature. Subsequent editions of this handbook[46] have a completely different section for the latent heat of evaporation. Again, even moderate variations in reported heats of vaporization can cause severe problems in calculating the polar (or hydrogen bonding) parameter when Equation 1.6 or Equation 1.8 are strictly adhered to.

CALCULATION OF THE HYDROGEN BONDING SOLUBILITY PARAMETER δ_H

In the earliest work, the hydrogen bonding parameter was almost always found by subtracting the polar and dispersion energies of vaporization from the total energy of vaporization. This is still widely used where the required data are available and reliable. At this stage, however, the group contribution techniques are considered reasonably reliable for most of the required calculations and, in fact, more reliable than estimating several other parameters to ultimately arrive at the subtraction step just mentioned. Therefore, in the absence of reliable latent heat and dipole moment data, group contributions are judged to be the best alternative. Similarity to related compounds can also be used, of course, and the result of such a procedure should be essentially the same as for using group contributions.

The above paragraph is not changed from the first edition of this handbook. This is to emphasize the importance of the work of Panayiotou and coworkers reported in Chapter 3. It now appears possible not only to calculate the hydrogen bonding parameter independently, but also to arrive at all three parameters by statistical mechanics. This is clearly a major step forward. Whether or not one understands all of the equations and methodology of Chapter 3, the procedure in itself confirms the need for (at least) three cohesion energy parameters, and similar results are found by the approach of the first paragraph as well as with statistical thermodynamics.

SUPPLEMENTARY CALCULATIONS AND PROCEDURES

The procedures listed previously are those most frequently used by the author in calculating the three partial solubility parameters for liquids when some data are available. There are a number of other calculations and procedures that are also helpful. Latent heat data at 25°C have been found consistently from those at another temperature, using the relation given by Fishtine.[47]

$$\Delta H_v(T_1)/\Delta H(T_2) = [(1 - T_{r1})/(1 - T_{r2})]^{0.38} \tag{1.14}$$

This is done even if the melting point of the compound being considered is higher than 25°C. The result is consistent with all the other parameters, and to date no problems with particularly faulty predictions have been noted. It appears as if the predictions are not significantly in error when experimental data are available for checking. When the latent heat at the boiling point is given in cal/mol, Equation 1.14 is used to estimate the latent heat at 25°C. RT equal to 592 cal/mol is then subtracted from this according to Equation 1.15, to find the total cohesion energy, E, in cgs units at this temperature:

$$E = \Delta E_v = \Delta H_V - RT \tag{1.15}$$

where R is the gas constant and T is the absolute temperature.

A computer program has been developed by the author to assign HSP to solvents, based on experimental data alone. This has been used in several cases where the parameters for the given liquids were desired with a high degree of accuracy. The procedure is to enter solvent quality, good or bad, into the program for a reasonably large number of polymers where the solubility parameters, and appropriate radius of interaction for the polymers are known. The program then locates that set of δ_D, δ_P, and δ_H parameters for the solvent that best satisfies the requirements of a location within the spheres of the appropriate polymers, that have good solvent quality, and outside the appropriate spheres where the solvent quality is bad.

An additional aid in estimating HSP for many compounds is that these parameters can be found by interpolation or extrapolation, especially for homologous series. The first member may not necessarily be a straight-line extrapolation, but comparisons with related compounds should always be made where possible to confirm assignments. Plotting the parameters for homologous series among the esters, nitroparaffins, ketones, alcohols, and glycol ethers has aided in finding the parameters for related compounds.

TEMPERATURE DEPENDENCE

Only very limited attempts have been made to calculate solubility parameters at a higher temperature prior to the second edition of this handbook. The inclusion of Chapter 3 and Chapter 10 in this handbook helps by providing a more accurate treatment of temperature dependence when the situation warrants it. Solubility parameter correlations of phenomena at higher temperatures have generally been found satisfactory when the established 25°C parameters have been used. Recalculation to higher temperatures is possible but has not generally been found necessary. In this direct but approximate approach, it is assumed that the parameters all demonstrate the same temperature dependence, which, of course, is not the case. It might be noted in this connection that the hydrogen-bonding parameter, in particular, is the most sensitive to temperature. As the temperature increases, more and more hydrogen bonds are progressively broken or weakened, and this parameter will decrease more rapidly than the others.

The gas-phase dipole moment is not temperature dependent, although the volume of a fluid does change with the temperature, which will also change its cohesive energy density. The change of the δ_D, δ_P, and δ_H parameters for liquids with temperature, T, can be estimated by the following equations, where α is the coefficient of thermal expansion[17]:

$$d\delta_D/dT = -1.25\alpha\delta_D \tag{1.16}$$

$$d\delta_P/dT = -0.5\alpha\delta_P \tag{1.17}$$

$$d\delta_H/dT = -\delta_H(1.22 \times 10^{-3} + 0.5\alpha) \tag{1.18}$$

Higher temperature means a general increase in rate of solubility/diffusion/permeation, as well as larger solubility parameter spheres. δ_D, δ_P, and δ_H decrease with increased temperature, as can be seen by a comparison of Equation 1.16, through Equation 1.18. This means that alcohols, phenols, glycols, and glycol ethers become better solvents for polymers of lower solubility parameters as the temperature increases. Thus, increasing the temperature can cause a nonsolvent to become a good solvent, a fact that is often noted in practice. As mentioned earlier, it is possible that a boundary solvent can be a good solvent at a given temperature, but turn bad with either an increase or a decrease in temperature. These phenomena are discussed in great detail by Patterson and coworkers.[3,4] They can be explained either by the change in solubility parameter with temperature or more completely by the Prigogine CST. The effects of temperature changes on solubility relations are most obvious with systems having a high hydrogen-bonding character. Examples are given in the next section for some special situations involving water and methanol.

SOME SPECIAL EFFECTS TEMPERATURE CHANGES

Water (and methanol) uptake in most polymers increases with increasing temperature. This is because the solubility parameters of the water and the polymer are closer at higher temperatures. The δ_H parameter of water (and methanol) falls with increasing temperature, whereas that of most polymers remains reasonably constant. Water is also well known as an exceptionally good plasticizer because of its small molecular size. The presence of dissolved water not only softens (reduces the glass transition temperature) a polymer as such, but it also means diffusion rates of other species will be increased. The presence of water in a film can also influence the uptake of other materials, such as in solubility parameter studies or resistance testing, with hydrophilic materials being more prone to enter the film.

This can cause blistering on rapid cooling as discussed in Chapter 12 and in Reference 48 (see Chapter 8 and Chapter 12). Figure 8.3 shows how rapid cooling from a water-saturated state at higher temperature can lead to blistering. Figure 12.3 and Figure 12.4 show how this effect can be measured experimentally with an increase in water content above the equilibrium value when temperature cycling is encountered. This leads to premature failure of polymeric products used in such environments.

A related problem has been encountered with methanol. It was intended to follow the rate of uptake of methanol in an epoxy coating at room temperature by weighing coated-metal panels periodically on an analytical balance. Blistering was encountered in the coating near the air surface shortly after the experiment began. The methanol that had been absorbed into the coating near the surface became insoluble as the temperature of the coating near the surface was lowered by the evaporation of excess methanol during the handling and weighing of the panels. This is a rather extreme case, and, as mentioned earlier, use of the HSP (determined at 25°C) at elevated temperatures can most often be done without too much trouble from a practical point of view. One should be aware that the changes in the δ_H parameter would be larger than those in the other parameters, and this effect would be most significant for those liquids with larger δ_H values.

EFFECTS OF SOLVENT MOLECULAR SIZE

The size of both solvent and solute molecules is important for solubility, permeation, diffusion, and chemical resistance phenomena. Smaller molecules tend to be more readily soluble than larger ones. As stated previously, the Hildebrand solubility parameter theory also points to smaller molar volume solvents as being better than those with larger molar volumes, even though they may have identical solubility parameters.[1,2] This fact of expected improved solvency for smaller molecules is also known from the Flory–Huggins theory of polymer solutions.[29] Solvents with smaller molecular size have also been repeatedly noted as being superior to those with larger molecular size, when highly crystalline polymers or solids are being tested for solubility. So it is not surprising

that solvent molecular size can be an important fourth parameter in solubility and, in some cases, in chemical resistance. Specific examples are given in Chapter 5 and Chapter 12.

The size and shape of the solvent molecule are also very important for kinetic phenomena such as diffusion, permeation, and attainment of equilibrium. Smaller and more linear molecules diffuse more rapidly than larger and more bulky ones. The diffusion coefficient may be so low that equilibrium is not attained for hundreds of years at room temperature. This was demonstrated in common solvent exposures of rigid polymers like polyphenylene sulfide (PPS) with thicknesses of several millimeters.[49] Likewise, the second stage in the two-stage drying process in polymer film formation by solvent evaporation can last for many years.[16,50] Polymer samples used for solubility parameter or other testing may well retain solvent or monomer for many years, and this may affect the evaluations.

Attempts to include the molecular volume in new composite solubility and size parameters have not been particularly successful.[20,21] This may be because the size effect is most often not caused due to the thermodynamic considerations on which the solubility parameters are based, but rather through a kinetic effect of diffusion rates or other free volume considerations. The similarities in the HSP approach and the Prigogine theory, discussed in Chapter 2, indicate a remarkably close, if not identical, relation between the Prigogine ρ (segment size parameter) and the δ_D parameter, suggesting that molecular size differences are at least partially accounted for in the δ_D parameter. The Prigogine theory also has a parameter to describe "structural effects," including size of polymer molecules, but this has not been explored in relation to the present discussion. The increase of δ_D with increasing molecular size among the aliphatic hydrocarbons, the higher δ_D values for the larger units represented by cycloaliphatic and aromatic rings, and the need for corrections for larger atoms discussed earlier tend to support the molecular size differences.

Sorting output data according to the molecular volume of the test solvents in a computer analysis helps to discover whether solvent molecular size is indeed an additional significant factor in a given correlation or testing program.

COMPUTER PROGRAMS

The author has used two computer programs extensively in his own studies and in collecting material for this book. These are called *SPHERE* and *SPHERE*1. They are very similar, the only difference being that SPHERE optimizes the polymer (or other material, of course) parameters based on all the data, whereas SPHERE1 considers data for only those solvents considered as "good." It neglects the nonsolvent data. SPHERE1 has been most useful in correlations with pigments, fillers, and fibers, as described in Chapter 7.

The data input is by solvent number followed by an indication of the quality of interaction with that solvent. A "1" indicates a "good" solvent, whereas a "0" is used for a "bad" solvent. What is considered good or bad varies according to the level of interaction being studied. This can be solution or not, a given percentage of swelling or uptake, breakthrough time being less than a given interval, permeation coefficients higher than a given value, long-time suspension of a pigment, etc.

The program systematically evaluates the input data using a quality-of-fit function called the *desirability function*.[51] This suggestion was made by a reputed statistician many years ago as the most appropriate statistical treatment for this type of problem. It has been in use since the late 1960s. The function has the form:

$$\text{DATA FIT} = (A_1 * A_2 * ... A_n)^{1/n} \tag{1.19}$$

where n is the number of solvents for which there is experimental data in the correlation. The DATA FIT approaches 1.0 as the fit improves during an optimization and reaches 1.0 when all the good solvents are included within the sphere and all the bad ones are outside the sphere.

$$A_i = e^{-(\text{ERROR DISTANCE})} \tag{1.20}$$

The A_i quotient for a given good solvent within the sphere and a bad solvent outside the sphere will be 1.0. The error distance is the distance of the solvent in error to the sphere boundary. It could either denote being good and outside the sphere or being bad and inside the sphere.

Ro is the radius of the sphere, and Ra is the distance from a given solvent point to the center of the sphere. For a good solvent outside the sphere, an error enters the DATA FIT according to:

$$A_i = e^{+(\text{Ro} - \text{Ra})} \tag{1.21}$$

Such errors are often found for solvents having low molecular volumes.

For a bad solvent inside the sphere, the contribution to the DATA FIT is

$$A_i = e^{+(\text{Ra} - \text{Ro})} \tag{1.22}$$

Such errors can sometimes be found for larger molecular species such as plasticizers. This is not unexpected for the reasons mentioned earlier.

Solvents with large and/or small molecules that give the "errors" can sometimes be (temporarily) disregarded by generating a new correlation; this gives an excellent DATA FIT for an abbreviated range of molecular volumes. There is a special printout with the solvents arranged in order of molecular volume that helps to analyze such situations. The computer printouts all include a column for the RED number.

The program assumes a starting point, based on an average of each of the HSP for the good solvents only. The program then evaluates eight points at the corners of a cube, with the current best values as center. Different radii are evaluated at each of these points in the optimization process. When better fits are found among the eight points, the point with the best fit is taken as a new center, and eight points around it are evaluated in a similar manner. This continues until the DATA FIT cannot be improved upon. The length of the edge of the cube is then reduced in size to fine-tune the fit. The initial length of the cube is 1 unit, which is reduced to 0.3 unit, and finally to 0.1 unit in the last optimization step.

Experimental data for the solvents are entered with solvent number (comma) and a "1" for a good solvent, or a "0" for a bad one.

Errors in the correlations are indicated with an "*" in the SOLUB column where the experimental input data are indicated. As stated above, systematic errors can sometimes be seen in the molar volume printout. This may suggest a new analysis of the data. Nonsystematic errors may be real, such as for reactions or some extraneous effect not predictable by the solubility parameter. They may also be bad data, and rechecking data indicated with an "*" in the output has become a routine practice. The output of this program is for the least radius allowing the maximum DATA FIT. An example is found in Table 5.4.

Results from the SPHERE program reported in this book generally include the HSP, given as D (δ_D), P (δ_P), and H (δ_H), respectively, and Ro for the correlation in question, as well as the DATA FIT, the number of good solvents (G), and the total solvents (T) in the correlation. This latter information has not always been recorded and may be lacking for some correlations, especially the older ones.

HANSEN SOLUBILITY PARAMETERS FOR WATER

Water is such an important material that a special section is dedicated to its HSP at this point. The behavior of water often depends on its local environment, which makes general predictions very difficult. Water is still so unpredictable that its use as a test solvent in solubility parameter studies

TABLE 1.3
HSP Correlations Related to Water

Correlation	δ_D	δ_P	δ_H	Ro	FIT	G/T
Water — Single molecule	15.5	16.0	42.3	—	—	—
Water — >1% soluble in[a]	15.1	20.4	16.5	18.1	0.856	88/167
Water — Total miscibility 1[a]	18.1	17.1	16.9	13.0	0.880	47/166
Water — Total miscibility "1[b]"	18.1	12.9	15.5	13.9	1.000	47/47

[a] Based on SPHERE program.
[b] Based on SPHERE1 Program.

is not recommended. This is true of water as a pure liquid or in mixtures. Table 1.3 includes data from various HSP analyses of the behavior of water. The first set of data is derived from the energy of vaporization of water at 25°C. The second set of data is based on a correlation of the solubility of various solvents in water, where "good" solvents are soluble to more than 1% in water. "Bad" solvents dissolve to a lesser extent. The third set of data is for a correlation of total miscibility of the given solvents with water. The second and third entries in Table 1.3 are based on the SPHERE program where both good and bad solvents affect the DATA FIT and hence the result of the optimization. The last entry in Table 1.3 is for an analysis using the SPHERE1 program. The HSP data are for the minimum sphere that encompasses only the good solvents. The bad solvents are simply not considered in the data processing. This type of comparison usually results in some of the parameters being lower than when all the data are included. A frequent problem is that a considerable portion of the HSP spheres, such as in the case for water, covers such high energies that no liquid can be found. The cohesion energy is so high as to require solids. The constant 4 in the correlations (Equation 1.9) is still used for these correlations, primarily based on successes at lower levels of cohesion energies, but this is also supported by the comparison with the Prigogine cst of polymer solutions, discussed at some length in Chapter 2. The HSP for water as a single molecule, based on the latent heat at 25°C is sometimes used in connection with mixtures with water to estimate average HSP. More recently, it has been found in a study involving water, ethanol, and 1,2-propanediol that the HSP for water indicated by the total water solubility correlation could be used to explain the behavior of the mixtures involved. The averaged values are very questionable as water can associate, and water has a very small molar volume as a single molecule. It almost appears to have a dual character. The data for the 1% correlation,[52] as well as for the total water miscibility, suggest that about six water molecules associate into units.

Traditionally, solvents are considered as points. This is practical and almost necessary from an experimental point of view as most solvents are so miscible as to not allow any experimental characterization in terms of a solubility sphere. An exception to this is the data for water reported in Table 1.3. The HSP reported here are the center points of HSP spheres where the good solvents are either those that are completely miscible or those that are miscible to only 1% or more, as discussed previously. It should also be mentioned that amines were a major source of outliers in these correlations. No solids were included. Their use to predict solubility relations for amines and for solids must therefore be done with caution.

CONCLUSION

This chapter has been dedicated to describing the tools with which different HSP characterizations can be made and some of the pitfalls that may be encountered in the process. The justification for
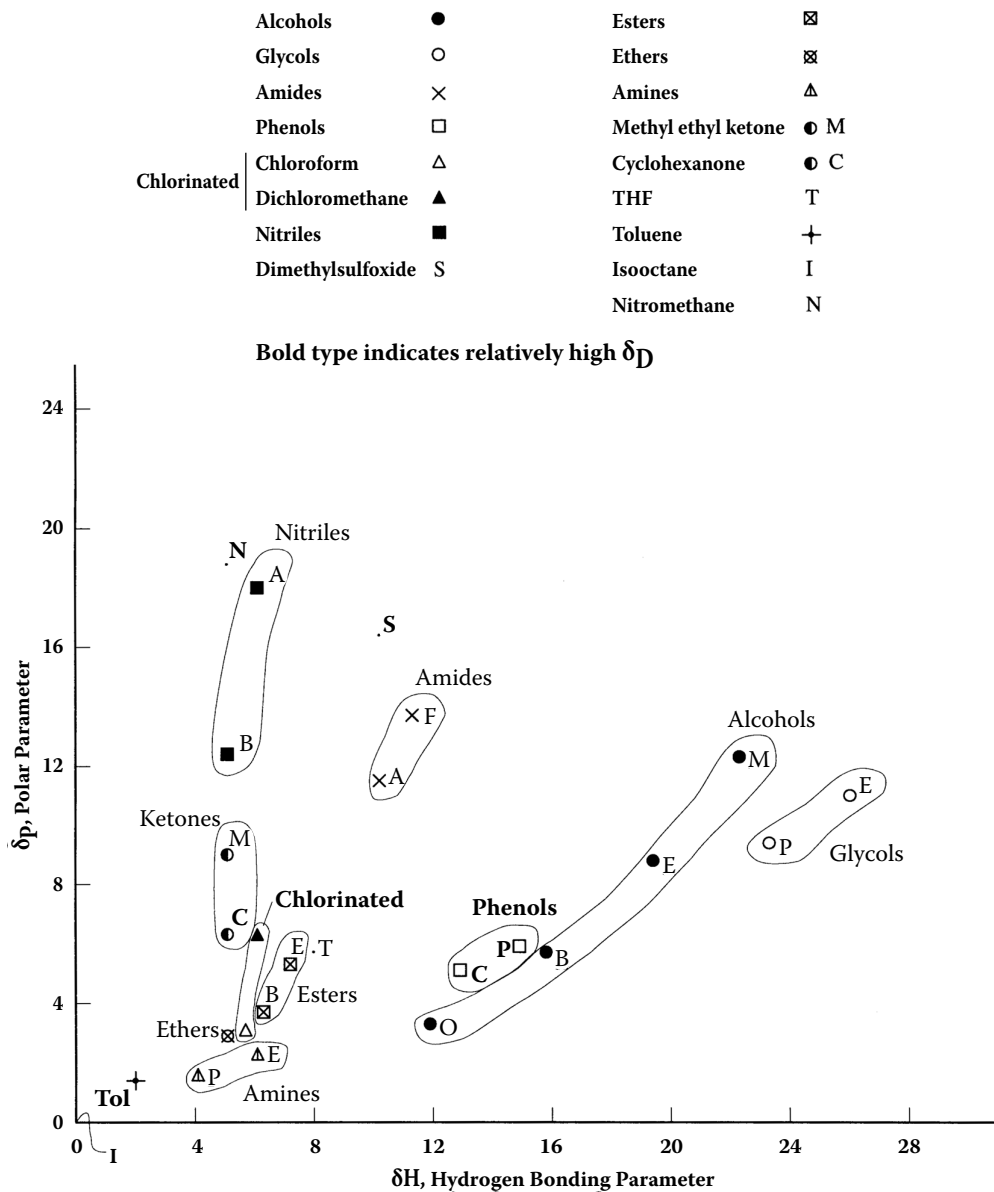
FIGURE 1.4 δ_p vs. δ_H plot showing the location of various common solvents. The glycols are ethylene glycol and propylene glycol. The alcohols include methanol (M), ethanol (E), 1-butanol (B), and 1-octanol (O). The amides include dimethyl formamide (F) and dimethyl acetamide (A). The nitriles are acetonitrile (A) and butyronitrile (B). The esters are ethyl acetate (E) and n-butyl acetate (B). The amines are ethyl amine (E) and propyl amine (P). The phenols are phenol (**P**) and m-cresol (**C**). The ethers are symbolized by diethyl ether.

the tools is further confirmed in Chapter 2 and Chapter 3, and their use is demonstrated in all the subsequent chapters. Figure 1.4 is included to show where many common solvents are located on a δ_p vs. δ_H plot.

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