Solubility Parameters

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Contents

I. Introduction

The nature of liquid mixtures may be interpreted in terms of molecular interactions broadly classified as either "reactive" (involving relatively strong "chemical" forces: complex formation, etc.) or "nonreactive" (involving relatively weak "physical" or "van der Waals" forces). Solution nonideality can of course be best explained if both "chemical" and "physical" forces are considered; the true situation is intermediate between these two extremes.[1] The solubility parameter approach is basically "physical", but introduction of specific interaction components has taken it some way toward a reasonably balanced position except where "solvation" is significant. This restriction usually limits it to nonelectrolyte solutions, but an extension to ionic systems is possible (see section IV.D).

General theories of the liquid state and solutions involve complex expressions linking the molecular interaction potential energy, thermal energy, and volume, and for many practical purposes it is convenient to use simpler, semiempirical methods. It has been found that a good solvent for a certain (nonelectrolyte) solute such as a polymer has a "solubility parameter" (δ, defined below) value close to that of the solute. Often a mixture of two solvents, one having a δ value higher and the other having a δ value lower than that of the solute is a better solvent than the two components of the mixture.

The basic assumption in the solubility parameter concept is

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TABLE I. Recent General Accounts of the Application of Solubility Parameters

Author	Country of publication	Language
Burrell[6-8,17,18]	USA	English
Cosaert[19]	Belgium	French and Flemish
Gardon[20]	USA	English
Geczy[a]	Hungary	Hungarian
Guzman[b]	Spain	Spanish
Hansen[13,21]	Denmark	English
Hansen[9-12,14]	USA	English
Hansen and Beerbower[22]	USA	English
Lucas[c]	France	French
Mandik and Stanek[d]	Czechoslavakia	Czech
Marti[e]	Switzerland	German
Nunn[23]	Belgium	English
Robu[f]	Romania	Romanian
Sandholm[24]	Finland	English
Seymour[g]	USA	English
Skaarup[25]	Denmark	English
Takada[h]	Japan	Japanese
Thomsen[i]	Denmark	Danish
Yoshida[j]	Japan	Japanese

[a] I. Geczy, *Kolor. Ert.*, **4**, 99 (1962); *Chem. Abstr.*, **61**, 4545b (1964). [b] G. M. Guzman, *Rev. Plast. Mod.*, **15**, 489 (1964); *Chem. Abstr.*, **63**, 13429g (1965). [c] M. T. Lucas, *Chim. Peint.*, **34**, 125 (1971); *Chem. Abstr.*, **75**, 78191 (1971). [d] L. Mandik and J. Stanek, *Chem. Prum.*, **15**, 223 (1965); *Chem. Abstr.*, **63**, 4509d (1965). [e] Θ. Marti, *Schweiz. Arch. Angew. Wiss. Tech.*, **33**, 297 (1967); *Chem. Abstr.*, **68**, 41006 (1968). [f] C. Robu, *Bul. Teh.-Inf. Lab. Cent. Cercet. Lacuri Cerneluri Bucuresti*, **57** (1969); *Chem. Abstr.*, **75**, 6364 (1971). [g] R. Θ. Seymour, *Austin Paint J., Austin, Finish. Rev.*, 13, 18 (1968); *Chem. Abstr.*, **68**, 88234 (1968). [h] M. Takada, *Hyomen*, **9**, 177 (1971); *Chem. Abstr.*, **75**, 133494 (1971). [i] E. S. Thomsen, *Farmaceuten*, **29**, 44 (1966). [j] T. Yoshida, *Shikizai Kyokaishi*, **44**, 186 (1971); *Chem. Abstr.*, **75**, 40973 (1971).

that there is a correlation between the cohesive energy density (potential energy per unit volume) and mutual solubility. The original definition[2-5] of the solubility parameter was in terms of the molecular cohesive energy ($-E$) per unit volume

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

but more recently multicomponent or so-called "multidimensional" solubility parameters have been evaluated by a variety of empirical methods. Although it may be more correct to define a solubility parameter in terms of internal pressure (section II.C), the above definition will be retained in this review. In the case of polymers a solubility parameter *range* is frequently more appropriate than a single value. The "molar cohesive energy" is frequently denoted E, but is here defined as $-E$, to conform with the usual sign convention.[3]

Solubility parameters and related properties such as internal pressure and cohesive energy density have proved useful in a great variety of applications (section X), and there have been many suggestions concerning both the methods of determination of solubility parameters and correlation with theoretical and thermodynamic parameters. In order to clarify the status of various parameters, it is necessary to distinguish clearly between (i) quantities which may be evaluated on a thermodynamic basis from measured properties such as pressure-volume-temperature (p–V–T) behavior and vaporization energy $\Delta_l^g U$, and (ii) parameters determined empirically by observation of the interaction between a liquid and a solid or another liquid.

In some cases it is reasonable to expect some kind of correlation between the thermodynamic quantities and empirical parameters, but such correlations should not be pursued too far.

Publications on solubility parameters fall fairly clearly into two categories: (i) practical chemistry, such as the coatings industry (typified by the work of Burrell[6-8] and Hansen[9-14]) and (ii) theory, initiated by Hildebrand[2-5] and Scatchard.[15,16] Interest in the former is increasing (as indicated, for example, by the number of recent papers, Table I) but in the latter is declining as attention has turned toward more sophisticated solution theories. This review attempts to present a balanced view of current attitudes to the subject and an indication of the extent to which the solubility parameter concept is applicable to real systems.

II. Thermodynamics

A. p–V–T Properties and Thermodynamic Equations of State

From basic thermodynamic relations there follows the "thermodynamic equation of state", linking pressure p, molar volume V, and temperature T:

$$(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p \tag{2}$$

Many liquids have values of $(\partial p/\partial T)_V$ and $(\partial U/\partial V)_T$ which within experimental accuracy are functions only of the molar volume, and because they show this simple behavior these functions have been given special names and symbols. The isothermal internal energy-volume coefficient $(\partial U/\partial V)_T$ is frequently called the internal pressure and given the symbol π (occasionally P_i) and the isochoric (constant volume) thermal pressure coefficient $(\partial p/\partial T)_V$ is denoted β. Thus

$$\pi = T\beta - p \tag{3}$$

The techniques[2-4,26-28] for evaluation of β and π have been applied to various liquids: polymers[29-32] and molten salts[33] as well as organic liquids[34-36] and liquid mixtures.[37] There is determined a set of those p–T values required to maintain a set quantity of liquid at a particular volume (i.e., a fixed density). The thermal pressure coefficient is determined from an isochoric p,T plot, and the internal pressure evaluated from eq 3. It follows that if β and π are functions of volume only, the p–T isochores are linear. For simple liquids at least, interesting comparisons with theory can be made: for example, if the internal pressure is identified with the attraction term in the van der Waals equation it follows that $1/\beta$ should be a linear function of the volume and this is observed in several liquids.[38]

The internal pressure approach was described and applied to liquids and liquid mixtures by Hildebrand and colleagues.[2-4,26] The internal pressure is the cohesive force which is the resultant of forces of attraction and forces of repulsion between molecules in a liquid, and considerable information can be gained by simply observing and comparing internal pressure-volume curves for pure liquids.[39] In addition to numerous studies of the relationship between internal pressure and cohesive energy density (section II.C), the effects of solvents on conformational equilibria have been expressed in terms of internal pressure.[40]

B. Cohesive Energy Density

In condensed phases (solids, liquids, solutions) strong attractive forces exist between molecules, and as a result each molecule has a considerable (negative) potential energy (in contrast with vapor phase molecules which have negligible potential energy). This potential energy is called the molar cohesive energy, $-E$.

It is customary to distinguish three modes of interaction between molecules which collectively produce the cohesive energy characteristic of the liquid state: (i) dispersion or London forces arising from the fluctuating atomic dipole which results from a positive nucleus and an electron cloud (this type of interaction occurs in all molecules); (ii) polar interactions, which can be further divided into dipole–dipole (Keesom) and dipole-induced dipole (Debye) interactions, resulting from nonuniform charge distribution; (iii) specific "chemical" interactions, notably hydrogen bonding.

The molar cohesive energy is the energy associated with all the molecular interactions in a mole of the material, i.e., $-E$ is the energy of a liquid relative to its *ideal* vapor at the same temperature (assuming that the *intra*molecular properties are identical in gas and liquid states, which may not be true in the case of complex organic molecules). It can therefore be seen that $-E$ consists of two parts: the energy $\Delta_l{}^gU$ required to vaporize the liquid to its saturated vapor, plus the energy required isothermally to expand the saturated vapor to infinite volume:

$$-E = \Delta_l{}^gU + \int_{V=V_{\mathrm{vap}}}^{V=\infty} (\partial U/\partial V)_T \mathrm{d}V \qquad (4)$$

At temperatures below the normal boiling point the second part may be neglected:

$$-E \approx \Delta_l{}^gU$$

and assuming ideal gas behavior,

$$-E \approx \Delta_l{}^gH - RT \qquad (5)$$

(A correction may be included for imperfection of the vapor if desired.) At higher temperatures the second term in eq 4 increases in relative importance, and at the critical temperature the first term is zero.

The cohesive energy density is defined as

$$c = -E/V \qquad (6)$$

where V is molar volume, and is thus approximately equal to the square of the solubility parameter:

$$\delta^2 = c \approx \Delta_l{}^gU/V \qquad (7)$$

C. Relationship between Cohesive Energy Density and Internal Pressure

This subject has been discussed in detail on several occasions (ref 3, 4, 15, 20, 35, 36, 41, 42) and is only briefly treated here. If the internal pressure is represented as the algebraic sum of "attractive" or positive and "repulsive" or negative terms (corresponding to negative and positive internal energy terms, respectively), it may be seen from a plot of internal pressure against volume for a typical liquid that at higher volumes (low pressures, high temperatures) the internal pressure may be approximately represented by the attractive term (subscript A) only. If it is assumed, as in the van der Waals equation (in which the repulsive energy is either 0 or $+\infty$), that

$$U = U_{\mathrm{A}} = AV^{-1} \qquad (8)$$

(where A is a proportionality constant), then

$$\pi = \pi_{\mathrm{A}} = -AV^{-2} = -U_{\mathrm{A}}V^{-1} \qquad (9)$$

The attractive part of the internal energy is equal to the vaporization energy at low gas pressure, so

$$(\partial U/\partial V)_T = \pi = \pi_{\mathrm{A}} = -U_{\mathrm{A}}/V = c = \Delta_l{}^gU/V = \delta^2 \qquad (10)$$

In general, however, c and π are not equal; c is a measure of the total molecular cohesion per unit volume (an integral quantity) while π is the instantaneous isothermal volume derivative of the internal energy. Thus, although the internal pressure provides one way of estimating the solubility parameter for simple liquids, this method is unsatisfactory for more complex molecules, and also for higher densities.

On the other hand, the internal pressure is a more satisfactory quantity than the solubility parameter to describe the macroscopic resultant of molecular interactions, because it is defined thermodynamically (eq 2) and it may be measured directly and precisely. For reasons such as these, Bagley and colleagues[36] (section IV.J) have chosen to define the solubility parameter for *nonpolar* liquids as

$$\delta^2 = \pi = (\Delta_l{}^gU/V) + \text{(correction term for internal degrees of freedom)} \qquad (11)$$

For *interacting* systems, on the other hand, two parameters are defined, one evaluated from the internal pressure and including the volume-dependent liquid state energy terms,

$$\delta_{\mathrm{v}}{}^2 = \pi \qquad (12)$$

and the other a residual solubility parameter,

$$\delta_{\mathrm{r}}{}^2 = (\Delta_l{}^gU - \pi V)/V \qquad (13)$$

This approach may well provide a satisfactory combination of practicality and theoretical rigor.

D. Conventions Relating to Symbols and Units

The symbols V, G, etc., are used here to denote molar volume, molar Gibbs energy, etc., i.e., the volume or Gibbs energy divided by amount of substance (number of moles) n. Partial molar quantities are denoted by X_{B}, where X is the extensive quantity and B is the chemical symbol for the substance:

$$X_{\mathrm{B}} = (\partial X/\partial n_{\mathrm{B}})_{T,p,n_{\mathrm{C}},\ldots} \qquad (14)$$

For a pure substance B the partial molar property X_{B} and the molar property are identical; this is denoted by $X_{\mathrm{B}}{}^*$, the superscript (*) indicating "pure".

The composition of a solution is usually described in terms of the *mole fraction*

$$x_{\mathrm{B}} = n_{\mathrm{B}} \Big/ \sum_{\mathrm{B}} n_{\mathrm{B}} \qquad (15)$$

or *volume fraction*

$$\phi_{\mathrm{B}} = n_{\mathrm{B}}V_{\mathrm{B}}{}^* \Big/ \sum_{\mathrm{B}} n_{\mathrm{B}}V_{\mathrm{B}}{}^* \qquad (16)$$

Except for "ideal solutions" (see below) the volume of a solution is not equal to the sum of the volumes of its components, but is the fractional sum of its partial molar volumes:

$$V(\mathrm{soln}) = \sum_{\mathrm{B}} x_{\mathrm{B}}V_{\mathrm{B}} \qquad (17)$$

The increase in any thermodynamic function X which accompanies the mixing of amounts n_{A} and n_{B} of two pure substances A and B is denoted $\Delta_{\mathrm{m}}X$:

$$\Delta_{\mathrm{m}}X(n_{\mathrm{A}},n_{\mathrm{B}}) = X(n_{\mathrm{A}},n_{\mathrm{B}}) - X(n_{\mathrm{A}},0) - X(0,n_{\mathrm{B}})$$

E. The Ideal Solution

The concept of the ideal solution is useful in describing the idealized limiting behavior of solution in the same way that the ideal gas laws describe the limiting behavior of gases. As shown in most general physical chemistry texts and by Hildebrand et al.,[3] for example, the thermodynamic definition of an ideal solution (a solution in which the activity equals the mole fraction over the entire composition range and over a nonzero range of temperature and pressure) leads to the following properties.

The *volume* of an ideal solution is equal to the sum of the volumes of the unmixed components, the temperature and pressure remaining constant:

$$\left(\sum_{\mathrm{B}} n_{\mathrm{B}}\right) V(\mathrm{soln}) = \sum_{\mathrm{B}} n_{\mathrm{B}}V_{\mathrm{B}}{}^* \qquad (18)$$

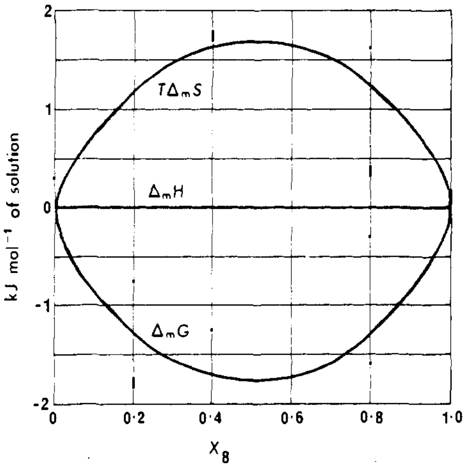

Figure 1. Changes in the thermodynamic functions $\Delta_m G$, $\Delta_m H$, and $T\Delta_m S$ for the formation of 1 mol of an ideal solution at 25°C (after "Physical Chemistry" by G. M. Barrow,[43] copyright 1973 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Co.).

or

$$V(\text{soln}) = \sum_B x_B V_B{}^* \tag{19}$$

The absence of volume change on mixing ($\Delta_m V = 0$) could be verified experimentally by dilatometry.

The *enthalpy* of an ideal solution is such that there is no change in the enthalpy of the system when the components are mixed at a fixed total pressure:

$$\Delta_m H = 0 \tag{20}$$

$$\left(\sum_B n_B\right) \Delta_f H^\circ(\text{soln}) = \sum_B n_B \Delta_f H^\circ\,(B) \tag{21}$$

or

$$\Delta_f H^\circ(\text{soln}) = \sum_B x_B \Delta_f H^\circ\,(B) \tag{22}$$

where $\Delta_f H^\circ$ denotes the standard enthalpy of formation. Experimentally there would be observed no temperature change in a thermally isolated system during dissolution.

The *entropy* change during the formation of an ideal gas mixture is

$$\Delta_m S = -R\sum_B x_B \ln x_B \tag{23}$$

and this is taken as the ideal entropy of solution for either gaseous or liquid solutions. The individual contribution associated with one component B is

$$S_B(\text{soln}) = S_B{}^\circ - R \ln x_B \tag{24}$$

The *Gibbs energy* of an ideal solution can be obtained by combining the enthalpy and entropy of mixing in a constant temperature-constant pressure process:

$$\Delta_m G = \Delta_m H - T\Delta_m S = RT\sum_B x_B \ln x_B \tag{25}$$

Therefore

$$\left(\sum_B n_B\right) \Delta G(\text{soln}) = \sum_B n_B[\Delta_f G(B) + RT \ln x_B] \tag{26}$$

$$\Delta G(\text{soln}) = \sum_B x_B[\Delta_f G(B) + RT \ln x_B] \tag{27}$$

and the individual component contributions are

$$\Delta G_B(\text{soln}) = \Delta_f G(B) + RT \ln x_B \tag{28}$$

To summarize, for an ideal dissolution process, $\Delta_m V = 0$, $\Delta_m H = 0$, and $\Delta_m S$ and $\Delta_m G$ are given by eq 23 and 25 and depicted in Figure 1. For nonideal solutions, deviation from the behavior shown in Figure 1 may be considerable, as illustrated in Figure 2 for carbon tetrachloride-methanol mixtures.[43]

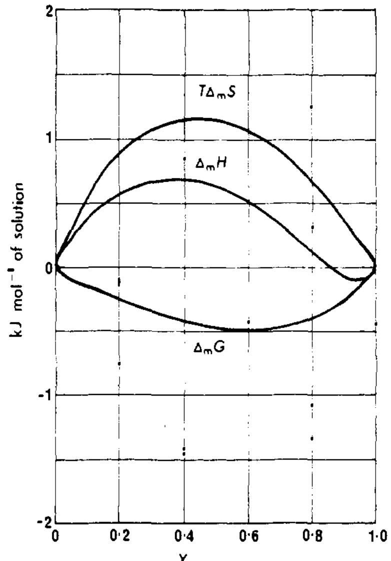

Figure 2. Changes in the thermodynamic functions $\Delta_m G$, $\Delta_m H$, and $\Delta_m S$ for the formation of 1 mol of carbon tetrachloride-methanol solution at 25°C (after "Physical Chemistry" by G. M. Barrow,[43] copyright 1973 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Co.).

F. Nonideal Solutions

In general the Gibbs energy of a component in a solution is not equal to its ideal value and the "excess" Gibbs energy of mixing is denoted G^E and defined

$$G^E = \Delta_m G - RT\sum_B (x_B \ln x_B) \tag{29}$$

(This may be considered either from the point of view of the *system* as the excess of the Gibbs energy of the nonideal solution over that of the ideal solution, or from the point of view of the *process* as the excess of the nonideal Gibbs energy of mixing over the ideal Gibbs energy of mixing.[3])

An alternative description of nonideality may be made in terms of activity and activity coefficient. Except for the special case of an ideal solution, the activity of a component is not equal to its concentration, and it becomes convenient to define the activity coefficient with symbol f_B for a component B of mole fraction x_B in a *mixture*. For *solutions* (when for convenience one of the substances, called the *solvent*, is treated differently from the *solutes*) the activity coefficient of solute B is described by γ_B on the molal scale and y_B on the concentration ("molar") scale.[44]

In terms of activity coefficients of the component B of a mixture,

$$\Delta_m G = RT\sum_B (x_B \ln x_B) + RT(x_B \ln f_B) \tag{30}$$

and

$$G^E = RT\sum_B (x_B \ln f_B) \tag{31}$$

Other thermodynamic excess functions are related to activity coefficients in the same way.

The Gibbs energy of mixing is in principle accessible from the partition function of the mixture, but this calculation is not practicable and approximate methods are used. The first step is usually to separate the Gibbs energy into enthalpy and entropy components:

$$\Delta_m G_p = \Delta_m H_p - T\Delta_m S_p \qquad (32)$$

the subscript p indicating a constant pressure process.

III. Theories of Solution

A. The Regular Solution

Perhaps the simplest of solution theories is based on the concept of a regular solution.[2,3]

"A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged" (Reprinted with permission from *J. Am. Chem. Soc.*, **51**, 69 (1929). Copyright by the American Chemical Society.)

In other words, a regular solution is one which despite a nonideal enthalpy of formation has an ideal entropy of formation. This can occur only if the random distribution of molecules persists even in the presence of specific solute–solvent interactions. Such a definition takes advantage of our ability to separate the Gibbs energy of solution formation into entropy and enthalpy components. The example usually quoted is for dissolution of iodine in various solvents, some yielding violet (nonsolvated, randomly mixed) solutions and others indicating by red color that specific (oriented) solvation and nonregularity is occurring.[2,3]

B. The Geometric Mean Assumption

For a pure liquid the cohesive energy density is defined by eq 6. For a mixture of components A and B it is necessary to define not only the cohesive energy density of molecules A or B surrounded by their own kind, but also that of a single A molecule in a B continuum or a single B molecule in an A continuum, c_{AB}. To estimate the value of c_{AB}, both Hildebrand[2] and Scatchard[15] used the geometric mean assumption:

$$c_{AB} = (c_{AA}c_{BB})^{1/2} \qquad (33)$$

This assumption was made on analogy with the result of London's simplified treatment of dispersion forces, which for molecules 1 and 2 at large separation was

$$u_{12} = (u_{11}u_{22})^{1/2}$$

where u is the potential energy of a pair of molecules. Inherent in this analysis is the assumption of molecular separation which is long compared with molecular diameters, neglect of polar and specific interactions, and omission of all but the first term in a series expansion. Also, u is a molecular quantity while c is a macroscopic quantity. It is therefore not surprising that the geometric mean expression often fails, nor that the direction and extent of deviation are unpredictable. The most that can be done is to empirically establish trends.

Deviations from the geometric mean have been discussed by Hildebrand et al.[3] in terms of an empirical binary coefficient, k_{AB}:

$$c_{AB} = (1 - k_{AB})(c_{AA}c_{BB})^{1/2} \qquad (34)$$

The effects of k_{AB} on the predictions of solubility parameter theory are greatest when $\delta_A \approx \delta_B$ (see below); k_{AB} tends to be zero or positive for nonpolar systems but negative when the components form complexes or have very different shapes.

Reed[45] and Thomsen[46] devised alternative corrections to the geometric mean rule in terms of "f-factors".

C. The Hildebrand–Scatchard Equation

Following van Laar's first attempt to treat the changes in entropy and enthalpy resulting from the mixing of liquids by using the van der Waals equation of state,[47] Scatchard[15] and Hildebrand[4,48] derived on semiempirical grounds an equation for the internal energy of mixing:

$$\Delta_m U_V = (x_A V_A^* + x_B V_B^*)(\delta_A - \delta_B)^2\phi_A\phi_B \qquad (35)$$

A simplified derivation emphasizing the physical significance has been published.[3]

Considering the partial molar energy of transferring a mole of liquid B from pure liquid to solution, and assuming a regular entropy of transfer, it follows[3] that the expression for the activity coefficient f_B of the solute resulting from the Hildebrand–Scatchard equation is

$$RT \ln f_B = V_B\phi_A^2(\delta_A - \delta_B)^2 \qquad (36)$$

There are several assumptions involved in the derivation of the Hildebrand–Scatchard equation.

(i) The geometric mean approximation is used so that $(\delta_A - \delta_B)^2$ can be written in place of $(c_{AA} + c_{BB} - 2c_{AB})$ which occurs in the more general form of the expression:

$$\Delta_m U_V = (x_A V_A^* + x_B V_B^*)(c_{AA} + c_{BB} - 2c_{AB})\phi_A\phi_B \qquad (37)$$

(ii) The constant pressure change of volume on mixing is assumed zero; the numbers of nearest neighbors of a molecule in solution and in the pure state are considered to be the same. The Hildebrand–Scatchard equation provides the constant volume internal energy of mixing, not the constant pressure enthalpy of mixing which one measures experimentally. Although these agree if there is no volume change on mixing, the effect of volume changes, which are particularly noticeable at high temperatures, is to produce a large disparity between $\Delta_m U_V$ and $\Delta_m H_p$.

(iii) It is assumed that the interaction forces act between the *centers* of the molecules.

(iv) It is assumed that the interaction forces are additive: the interaction between a pair of molecules is not influenced by the presence of other molecules.

(v) It is assumed that the mixing is random: neither A–B, A–B, nor B–B nearest neighbor situations is favored, and the distribution is temperature independent.

These assumptions are of course not generally valid, but produce an equation which is simple and convenient to use as a starting point for empirical or semiempirical expressions. Implicit in the Hildebrand–Scatchard equation is the assumption that the quantity $(-EV)^{1/2}$ is additive. Not only does it appear to be additive on a solute–solvent basis, but this is true also to some extent for groups within organic molecules and polymers.[16] Such additive constants have been named molar attraction constants (section IV.G).

D. Gibbs Energy of Mixing

For dissolution to be possible the Gibbs energy of mixing for a constant pressure process (eq 32) must be negative, and this may be achieved by reducing $\Delta_m H_p$. If $\Delta_m H_p$ is negative, or positive and less than $T\Delta_m S_p$, mixing can occur. Spontaneous "unmixing" (separation into two phases) can occur when the thermodynamic stability conditions are exceeded, although it is possible for metastable homogeneous systems to exist.[49] The discussion above on the Hildebrand–Scatchard equation shows that for *nonpolar liquids* this is equivalent to reducing the quantity $(\delta_A - \delta_B)^2$. For *polar liquids and solids* it has been assumed that the same principle holds; that is, similarity in solubility parameter values provides a more negative Gibbs energy of mixing. This assumption has proved reasonably satisfactory in practice, although no detailed theory has been developed for this important aspect of solubility parameters.

It has been usual in simple one-component solubility parameter treatments to assume that $\Delta_m S$ is ideal; i.e., it is assumed that the solution is regular. In terms of excess quantities, the Hildebrand–Scatchard equation provides U_V^E, and from

$$\Delta_m A_V = \Delta_m U_V - T\Delta_m S_V \qquad (38)$$

A_V^E may be evaluated (assuming $S_V^E = 0$). When account is taken of the volume change on mixing, H_p^E and G_p^E are obtained. This procedure provides values for G_p^E which are in reasonable agreement with experiment (primarily direct calorimetric measurement of the mixing process), but this appears to be due to a cancellation of errors in U_V^E and S_V^E which arise from the Hildebrand–Scatchard assumptions. The existence of changes in noncentral degrees of freedom (vibration and rotation) in the mixing process can be shown to have a considerable (but similar) effect on TS_V^E and U_V^E.

The second energy term in eq 32 and 38 is the product of entropy and temperature: entropy may be considered as describing the type of motion, so a certain amount (described by the temperature) of molecular motion carried out in a certain way (described by the entropy) represents a certain energy.[50]

E. The Flory–Huggins Equation

Flory[51,52] and Huggins[53] were the first to calculate the entropy of mixing of long-chain molecules with the assumption that segments occupied sites of a "lattice" and solvent molecules occupied single sites. They proposed the polymer–solvent interaction parameter χ, a dimensionless quantity characterizing the difference in interaction energy of a solvent molecule immersed in pure polymer compared with one in pure solvent. Thus a good solvent has a low χ value. The expression for the Gibbs energy of mixing is

$$\Delta_m G/RT = x_A \ln \phi_A + x_B \ln \phi_B + \chi\phi_A\phi_B(x_A + V_B x_B/V_A) \qquad (39)$$

where x denotes mole fraction, ϕ denotes volume fraction, the subscript B denotes the polymer component, and χ is the Flory interaction parameter for that particular solute–solvent pair. The first two terms result from the configurational entropy of mixing and are always negative. For $\Delta_m G$ to be negative (i.e., for the polymer to be soluble) X must be either negative, or positive and small. The critical value when V_B/V_A is large is $\chi \leq 0.5$ for solubility throughout the entire range of composition.

The Flory interaction parameter contains both entropy and enthalpy contributions, and so can be expressed as

$$\chi = \chi_S + \chi_H$$

and χ_H is frequently calculated from the Hildebrand–Scatchard regular solution theory (eq 35). Empirically, χ_S is usually between 0.2 and 0.6, so χ_H must be small, and consequently δ_A and δ_B must be very similar for polymer solubility according to this criterion.[20,49,54,55] It appears that the Flory–Huggins theory is of some value in considering the thermodynamics of dilute solutions, but according to one school of thought it is of limited help in solvent formulation problems.[7] Its shortcomings as a practical solubility criterion include the following: (i) it is concentration-dependent, (ii) it is not easily evaluated experimentally, (iii) it is a composite term influenced by hydrogen bonding, (iv) it has no sound theoretical basis, (v) it is inconvenient for multicomponent systems because interactions between each pair of components must be known. Nevertheless the polymer–solvent interaction parameter is still used extensively, and comprehensive compilations of values have been published, for example, ref 56.

F. Statistical Thermodynamics

A more strictly correct (but often less practically useful) approach to the liquid state is provided by statistical thermodynamics: it is possible in principle to calculate thermodynamic properties from partition functions for a system of known molecular properties.[27,47,57–61] Although information from this approach is largely limited to "simple" systems in which dispersion forces predominate, it does draw attention to the problem of the entropy of mixing which was introduced above (section III.D) and does explain aspects of the effect of molecular parameters on the excess thermodynamic functions. These theoretical approaches are not discussed here.

G. Other Solution Theories

The regular solution approach attempts to explain solution nonideality in terms of *physical* intermolecular forces. The same is true of the lattice theories, which consider a liquid to be quasi-crystalline, and the corresponding states theories which consider that the residual properties should coincide when plotted with reduced coordinates.

The other theories are of the *chemical* type, with the assumption that molecules in a liquid solution interact to form new chemical species with resulting nonideality. They include the concepts of association, solvation, Lewis acid-base properties, hydrogen bonding, and electron donor–acceptor complexes. These theories have been reviewed widely and will not be discussed here.

Thomsen[46] has compared the corresponding states approach of Prigogine and the solubility parameter theory of Hildebrand. Burrell[18] has summarized recent theoretical trends in polymer solvation, including molecular clustering theories based on aggregation or entanglement of polymer molecules even in "good" solvents.

IV. The Solubility Parameter Philosophy

A. The Hildebrand, Regular, or One-Component Solubility Parameter

The one-component solubility parameter defined by eq 1 has proved useful for regular solutions, i.e., solutions without molecular polarity or specific interactions, and good estimates of excess Gibbs energy (and consequently activity coefficients, etc.) have been obtained because of a fortuitous cancellation of errors. It is still used for various purposes in nonregular solutions, but to some extent has been superseded by multicomponent solubility parameters (see below).

It has been usual to evaluate the total solubility parameter

$$\delta_0 = \left(\sum_i \delta_i^2\right)^{1/2} \qquad (40)$$

where the δ_i are the empirical estimates of the various contributions from dispersion forces, polar forces, and hydrogen bonding, and to call this simply the solubility parameter. Although δ_0 may be compared with $\delta = (\Delta_l{}^g U/V)^{1/2}$, the two quantities in general should not be expected to be equal, and it is therefore preferable to reserve the use of the symbol δ for the thermodynamically determined $(\Delta_l{}^g U/V)^{1/2}$ and not to confuse it with the empirically determined δ_0 values.

B. Units

It is usual practice at present to express the internal pressure in pressure units (preferably the pascal, 1 Pa = 1 Nm^{-2}) and to express cohesive energy density in energy density units (Table II), but as these are dimensionally identical it would be more convenient to use a common unit. The megapascal, MPa, is a suitable choice.

Perhaps because solubility parameters are more widely

TABLE II. Cohesive Energy Density and Internal Pressure Units and Conversion Factors

	cal cm^{-3}	J cm^{-3} ≡ MPa	atm	bar	kg cm^{-2}
1 cal cm^{-3}	1	4.1840	41.293	41.840	42.665
1 J cm^{-3} ≡ 1 MPa	0.23901	1	9.8692	10.000	10.1972
1 atm	0.024217	0.101325	1	1.01325	1.03323
1 bar	0.023901	0.10000	0.98692	1	1.01972
1 kg cm^{-2}	0.023439	0.098066	0.96784	0.98067	1

TABLE III. Solubility Parameter Units and Conversion Factors

	cal$^{1/2}$ cm$^{-3/2}$	J$^{1/2}$ cm$^{-3/2}$ ≡ MPa$^{1/2}$	atm$^{1/2}$
1 cal$^{1/2}$ cm$^{-3/2}$	1	2.0455	6.4260
1 J$^{1/2}$ cm$^{-3/2}$ ≡ 1 MPa$^{1/2}$	0.48888	1	3.1415
1 atm$^{1/2}$	0.15562	0.31832	1

used by applied chemists than by pure chemists, the SI convention of units has not been adopted, and even recently the suggestion has been made[62] and supported[22,63] to adopt as title for the non-SI unit cal$^{1/2}$ cm$^{-3/2}$ the "hildebrand". Following on from the argument above, the most appropriate and convenient multiple unit is the MPa$^{1/2}$ (see Table III), which is numerically equal to the J$^{1/2}$ cm$^{-3/2}$.

C. Polar Effects

The cancellation of errors (section III.D) which permits the Hildebrand–Scatchard theory and regular solubility parameters to be used for nonpolar solutions would not be expected to occur in the presence of polar interactions. In particular the cohesive energy of a polar liquid is due to polar forces as well as dispersion forces, and the geometric mean assumption (section III.B) is unlikely to apply to the portion of the cohesive energy density resulting from polar forces.

It has long been apparent that to be generally useful a solubility parameter theory must deal with polar contributions by providing information about the *nature* of the interactions between molecules as well as the *total strength* of the interactions. One method[55] is to define a *fractional polarity* as the fraction p of total interactions due to dipole–dipole effects, the remainder being due to dispersion (d) and induction (in) effects:

$$p + in + d = 1 \qquad (41)$$

More generally, two-component solubility parameters have been developed[54,64] with polar (τ) and nonpolar (λ) components:

$$-E/V = -E_{\mathrm{nonpolar}}/V - E_{\mathrm{polar}}/V \equiv \lambda^2 + \tau^2 \qquad (42)$$

The expression ($c_{AA} + c_{BB} - 2c_{AB}$) in the general form of the Hildebrand–Scatchard relation (eq 37) is not simply $(\delta_A - \delta_B)^2$ because the geometric mean assumption applies only to λ. Keller et al.[65] have emphasized that polar interactions are of two types. Polar molecules, those molecules possessing permanent dipole moments, interact in solution by dipole *orientation* (sometimes referred to as Keesom interactions) in a "symmetrical" manner; i.e., each of a pair of molecules interacts by virtue of the same property. It follows that the geometric mean rule is obeyed for orientation interactions and the contribution of dipole orientation to cohesive energy as for dispersion interactions. On the other hand, dipole *induction* interactions are "unsymmetrical", involving the dipole moment of one molecule with the polarizability of the other. Thus in a pure polar liquid without hydrogen bonding

$$\delta_o^2 = \delta_d^2 + \delta_{or}^2 + 2\delta_{in}\delta_d \qquad (43)$$

where subscripts d, or, and in refer to dispersion, orientation, and induction. Nevertheless δ_{in} must be related to δ_{or}, and a single parameter, δ_p, is frequently used for all polar interactions.

D. Extension to Ionic Systems

In chemical systems which contain ions, polar effects usually outweigh all other effects. Although dipole moments and relative permittivities cease to be appropriate measures of polarity for solubility parameter estimation, the cohesive energy density or solubility parameter may remain a useful criterion. Hansen[9] has characterized inorganic salts by his three-component solubility parameter system. Gordon[66,67] has discussed measures of polarity in connection with molten salts as solvents, pointing to E_η/V (E_η being the activation energy for viscous flow)[68] and the Kosower Z value[69] as suitable polarity scales for the range of solvents from monatomic liquids to molten metals. In particular, molten organic salts seem to span a range of solvent properties from those comparable to the highly cohesive molten inorganic salts to those of the very low cohesive energy density hydrocarbons. At this lower end of the scale lie the quaternary ammonium salts $R_4N^+X^-$ which apparently owe their small cohesive energy densities to their large ionic volumes. It is of interest that even in some of these ionic systems (e.g., the thiocyanates and R_3NH^+picrate$^-$) hydrogen-bonding energy still influences the cohesive energy.

In liquids of relative permittivity below about 30, there is evidence[70,71] that univalent ions are largely undissociated and it might therefore be expected that solubility parameter concepts could be extended directly to such cases. The solubility of sodium salicylate in a series of pure alcohols shows a maximum at 1-pentanol (relative permittivity 13.9) similar to the corresponding figure for salicylic acid (15), indicating that sodium salicylate is behaving essentially as a nonelectrolyte.[71] The solubilities of amine salts in low polarity solvents[72] and ion-association extraction systems[73] have also been considered from the solubility parameter point of view.

E. Specific Interactions (Hydrogen Bonding)

Burrell,[6,8] who was one of the first to deal with the hydrogen-bonding problem in solubility parameters, divided solvents into three classes according to their hydrogen bonding capacity: *poor*, including hydrocarbons, chlorinated hydrocarbons, and nitrohydrocarbons; *moderate*, including ketones, esters and ethers; *strong*, such as alcohols. This classification method is still widely used in practical applications and is included in Table V (section VII.B).

Lieberman[74] developed the idea, assigned arbitrary quantitative values to these groups, and plotted two-dimensional graphs of solubility parameters against hydrogen-bonding capacities. This technique proved useful and was made more reliable by the introduction[63] of a direct hydrogen-bonding parameter using a spectroscopic criterion based on the work of Gordy and Stanford.[75] The extent of the shift to lower frequencies of the OD infrared absorption of deuterated methanol provided a measure of the hydrogen-bonding acceptor power of the liquid under study. The spectrum of a so-

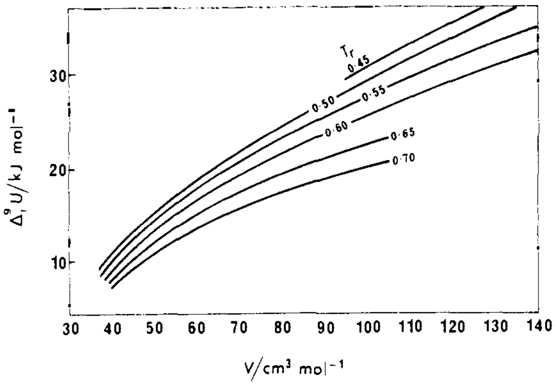

Figure 3. Vaporization energy $\Delta_l{}^gU$ for straight-chain hydrocarbons (after Blanks and Prausnitz[54] and used with permission of the American Chemical Society).

lution of deuterated methanol in the test solution was compared with that of a solution in benzene, and the hydrogen-bonding parameter was defined

$$\gamma = \Delta\nu/10 \qquad (44)$$

when the OD absorption shift $\Delta\nu$ was expressed in wavenumbers.

Crowley et al.[83] applied this technique, and more precise measurements were made by Nelson et al.[76] who also discussed the choice of reference solvent; benzene is, in fact, a weak hydrogen bond acceptor, and there is even a small amount of hydrogen bonding between methanol and carbon tetrachloride. Methanol in cyclohexane appears to be the best reference system.

All these approaches to the hydrogen-bonding parameter problems failed to include the fact that hydrogen bonding is an unsymmetrical interaction, involving a donor and an acceptor with different roles rather than two equivalent mutually hydrogen-bonding species. The energy of a hydrogen-bonding interaction is the product of a function of the hydrogen bond accepting capability ($\mathcal{A}$) and the hydrogen bond donating capability ($\mathcal{D}$).[18,49,58,77] This may be written

$$\Delta H_h = \phi_A\phi_B(\mathcal{A}_A - \mathcal{A}_B)(\mathcal{D}_A - \mathcal{D}_B) \qquad (45)$$

and it is apparent that the maximum interaction occurs when $\mathcal{A}_A = \mathcal{D}_B = 0$ or $\mathcal{A}_B = \mathcal{D}_A = 0$. Both Keller et al.[65] and Nelson et al.[76] utilized this approach to hydrogen bond solubility parameters. The effective or net hydrogen bond accepting ability of a solvent mixture, introduced by Nelson et al.,[76] recognizes the fact that, for example, when alcohols are diluted, hydrogen bonds are broken, the hydrogen bond accepting ability is reduced, and so the contribution of alcohols to the net hydrogen bond accepting ability is negative.

An alternative to the "physical" approaches outlined above is the quasi-chemical approach; e.g., alcohols in non-hydrogen-bonding solvents may be considered as linear polymer complexes.[78-80] Harris and Prausnitz[1] have combined chemical and physical interaction treatments of solvating binary liquid mixtures.

In pharmaceutical applications hydrogen bonding solvents are of great importance, and use has been made[81,82] of the fact that in such solvents there is a good correlation between solubility parameters and relative permittivities.

F. The Homomorph or Hydrocarbon Counterpart Concept

In any multicomponent solubility parameter system there arises the problem of evaluating the nonpolar component. Brown et al.[83] proposed the homomorph concept: the homomorph of a polar molecule is a nonpolar molecule having very nearly the same size and shape as the polar molecule. This was applied to the vaporization energy of polar and hydrogen-bonded liquids by Bondi and Simkin[84] and many subsequent workers including Prausnitz and coworkers[54,64] and Helpinstill and Van Winkle.[85]

The nonpolar component of the vaporization energy of a polar liquid is taken as the experimentally determined total vaporization energy of the homomorph at the same reduced temperature (the actual temperature divided by the critical temperature, both on the absolute temperature scale). The molar volumes should also be equal for this comparison. If it is available, information on the molar volumes of a range of the hydrocarbon homomorphs enables the molar volume of the polar liquid to be used as an independent variable so that dispersion energy density at any desired molar volume and reduced temperature can be determined (see Figure 3). Different plots are used for straight-chain, cyclic, and aromatic hydrocarbons. If the vaporization energies for the appropriate hydrocarbons are not available, they may be evaluated by one of the methods discussed in section V.A.

Hansen and Beerbower[22] have pointed out inaccuracies in the homomorph charts of ref 64 and 85, and have recommended the use of the chart of Blanks and Prausnitz[54] which has been the basis for several successful correlations. Keller et al.[65] have recommended an alternative, more fundamental approach to predicting dispersion contributions, based on a relationship between δ_d and the Lorentz-Lorenz function, $(n^2 - 1)/(n^2 + 2)$, n being the refractive index (section V.B).

G. Solubility Parameters of Functional Groups: Molar Attraction Constants

Scatchard[15] and Small[49] pointed out the additivity of $(-EV)^{1/2}$ which follows from the geometric mean assumption, showed that in several homologous series $(-EV)^{1/2}$ was linear with the number of carbon atoms, and proposed molar attraction constants F which were additive constants for the common organic functional groups. Cohesive energies and solubility parameters could then be estimated for any molecule:

$$-E = \frac{(\Sigma F)^2}{V};\ c = \left(\frac{\Sigma F}{V}\right)^2;\ \delta = \frac{\Sigma F}{V} \qquad (46)$$

The method cannot be used directly for compounds in which hydrogen bonding is significant (hydroxyl compounds, amines, amides, carbocyclic acids).

Konstam and Feairheller[86] proposed an alternative method for calculating solubility parameters (and molar volumes) of functional groups. In general, straight lines resulted when the solubility parameters $\delta = (-E/V)^{1/2}$ of a homologous series of monofunctional compounds were plotted against the reciprocal of their molar volumes V. (This is equivalent to plotting $(-EV)^{1/2}$ against the number n of carbon atoms if V is a linear function of n.) This method is more satisfactory for calculating the solubility parameters of high molecular weight members of a homologous series from data on low molecular weight members.

Hoy[87] also expanded Small's method and in addition introduced the concept of "chameleonic" materials which adopt the character of the surrounding environment, for example, by dimerization (e.g., carboxylic acids) or intramolecular hydrogen bonding (e.g., glycol ethers). In polar or hydrogen bonding solvents respectively these materials act in the appropriate fashion, but in other solvents the polar or hydrogen bonding interactions are intramolecular.

Rheineck and Lin[88] have proposed a correction for molar volumes in functional group behavior. Both the cohesive energy $-E$ and the molar volume V of a given substance were found to be the sum of individual contributions from chemical groups

$$-E = \Sigma -E_i;\ V = \Sigma V_i \qquad (47)$$

and E_i and V_i were almost independent of molecular size. Consequently they defined

$$\delta = (-E/V)^{1/2} = (\Sigma -E_i/\Sigma V_i)^{1/2} \qquad (48)$$

Hansen and Beerbower[22] extended the functional group concept to partial solubility parameters, observing that $V\delta_p$ and $V\delta_h{}^2$ provided the most satisfactory basis for evaluating group contributions, although the "chameleonic" effect still prevents free additive use of these functions.

H. Three-Component Solubility Parameters

A three-component system based on the division of intermolecular forces into dispersion, polar, and hydrogen bonding parts was introduced by Crowley, Teague, and Lowe.[63,89] One axis represented the regular or Hildebrand solubility parameter δ, another polar effects (in terms of dipole moment μ), and the third hydrogen bonding (in terms of the spectroscopic parameter γ defined in section IV.E). Volumes of solubility could then be determined experimentally and drawn up in three dimensions (Figure 4) and represented in two dimensions by a contour diagram (Figure 5). Some solutes, notably cellulose nitrate, showed a significant region of borderline solubility (gel formation) representing "wall-thickness" in the three-dimensional model.

Hansen[10-13,21,22] also proposed that the concept of the solubility parameter could be extended to polar and hydrogen bonding as well as dispersion interactions. This solubility parameter vector approach avoided the arbitrary axes of μ and γ, and by doubling the scale on the dispersion axis approximately spherical volumes of solubility could be drawn up for any solute (see below). It was assumed that dispersion, polar, and hydrogen-bonding parameters were simultaneously valid, their particular values being determined by a large number of experimental solubility observations.

A rationalization for the three-component solubility parameter concept may be made on the following basis. It is assumed that the cohesive energy $-E$ arises from contributions from hydrogen bonding or similar specific interactions $-E_h$, polar interactions $-E_p$, and nonpolar or dispersion interactions $-E_d$

$$-E = -E_d - E_p - E_h \qquad (49)$$

$$-E/V = -E_d/V - E_p/V - E_h/V$$

or

$$\delta_0{}^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2 \qquad (50)$$

These individual solubility parameters are evaluated by experimental solubility observations (section V). As emphasized above (section IV.A), the total solubility parameter δ_0 evaluated from the empirical values of the individual solubility parameters should not be expected to be identical with $(\Delta_l{}^gU/V)^{1/2}$. Sometimes δ_p and δ_h (the association interactions) are collectively described as

$$\delta_a = (\delta_h{}^2 + \delta_p{}^2)^{1/2} \qquad (51)$$

This is equivalent to the "polar solubility parameter" τ of Blanks and Prausnitz.[54] An estimate of δ_a is available from the difference between δ^2 $(=\Delta_l{}^gU/V)$ for the liquid and for its homomorph. Nunn[23] has published numerical examples of the practical application of the three-component parameters of Crowley et al. and of Hansen. Hansen's three-dimensional treatment has the advantage that the three components have the same units and if the δ_d scale is expanded by a factor of 2, a *spherical* solubility volume for a solute may be drawn with a suitable radius and compared with the point locations of solvent. The solvent locations may be considered as true vector quantities, in contrast to Crowley's parameter. Burrell[7] has reminded us that these methods tend to distort the relative magnitudes of the intermolecular forces, the polar contribution to cohesive energy density being usually small in relation to that of hydrogen bonding in mixtures where hydrogen bonds can form.

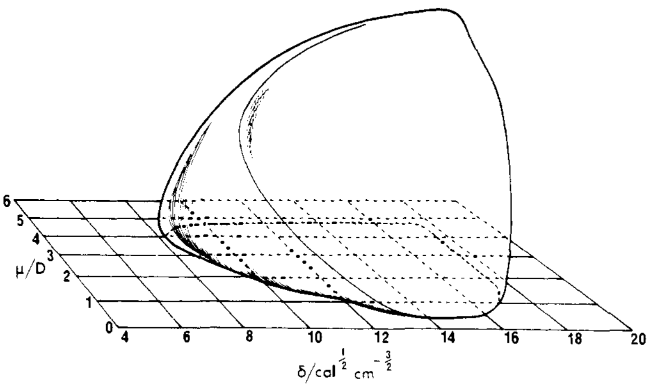

Figure 4. Solid model representation of cellulose nitrate solubility in terms of Hildebrand solubility parameter δ, dipole moment μ, and (vertical axis) the spectroscopic parameter γ (from Crowley et al.[63] with the permission of the *Journal of Paint Technology*).

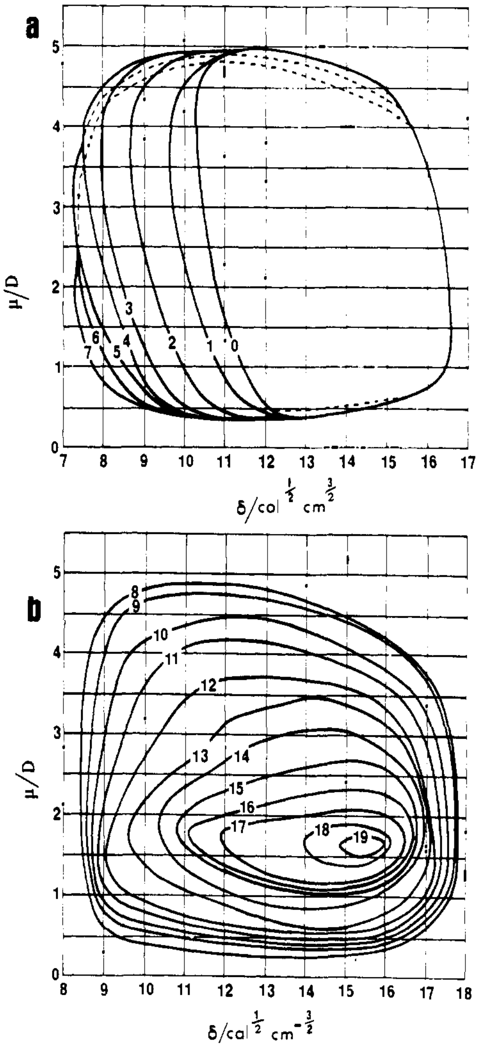

Figure 5. Solubility map of cellulose nitrate: (a) $\gamma = 0$ to 7, (b) $\gamma = 7$ to 19 (from Crowley et al. [89] with the permission of the *Journal of Paint Technology*).

As pointed out in section IV.E, it is necessary to distinguish between the hydrogen-bonding accepting and donating properties of liquids, and to make allowance for the fact that a hydrogen bond requires both a molecule capable of donating a proton and a molecule capable of accepting one. This fact was incorporated in the three-component method of Nelson et al.[76,90] with Hildebrand solubility parameter, fractional polarity, and net hydrogen bonding index.

I. Triangular Representation

Teas[91] showed that for several polymer–solvent systems it was possible to use fractional cohesive energy densities plotted on a triangular chart to represent solubility limits:

$$E_d = \frac{\delta_d^2}{\delta_0^2},\ E_p = \frac{\delta_p^2}{\delta_0^2},\ E_h = \frac{\delta_h^2}{\delta_0^2} \tag{52}$$

where

$$\delta_0^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

so

$$E_d + E_p + E_h = 1 \tag{53}$$

This method was used by Vial,[92,93] but Teas chose to use fractional parameters defined as

$$f_d = \frac{100\delta_d}{\delta_d + \delta_p + \delta_h},\ f_p = \frac{100\delta_p}{\delta_d + \delta_p + \delta_h},\ f_h = \frac{100\delta_h}{\delta_d + \delta_p + \delta_h} \tag{54}$$

This had the advantage of spreading the points more uniformly over the triangular chart, but the disadvantage that it was completely empirical, without even the limited theoretical justification of regular solution theory.

These approaches make the single simplifying assumption that the total solubility parameter δ_0 is constant, and that it is the relative magnitude of the three types of forces which determine the dissolving ability of a solvent. In general δ_0 values decrease regularly with increasing E_d or f_d, indicating the dominating contribution to δ_0 of polar and hydrogen bonding forces in most liquids.[91]

J. Two-Component (Physical-Chemical) Solubility Parameters

The relationship between solubility parameter, cohesive energy density, and internal pressure has been considered by a number of research groups. Recent information from one of these[36,42,78,94,95] indicates that two-component solubility parameters based on "physical" (polar and nonpolar) and "chemical" effects may be superior to three-component systems. One term, δ_v, includes the volume-dependent terms in the liquid energy expression and corresponds to the physical polar and nonpolar effects. It is derived by experiment directly from the internal pressure, eq 12. The other term is the residual solubility parameter δ_r, eq 13, arising from chemical (notably hydrogen-bonding) effects.

This approach has the advantage of utilizing thermodynamic quantities π and Δ_l^gU which are fairly readily available for most solvents (although not for solutes) in contrast to the Hansen parameters which are empirically determined. Considerable agreement would be expected between the values of δ_v^2 and $\delta_d^2 + \delta_p^2$ and between the values of δ_r and δ_h, but because both types of parameter are based on simplified concepts, there is no reason to expect them to be identical. It appears that it is more appropriate to couple δ_d and δ_p in this way than to combine polar and hydrogen-bonding terms.[36]

In a similar manner Chen[96] has combined the Flory interaction parameter (which takes into account the dispersion and polar interactions) with the hydrogen-bonding solubility parameter to develop a two-component approach to polymer miscibility.

K. The Solubility Parameter as a Zeroth Approximation for Excess Gibbs Energy

The solubility parameter concept has been described[2] as only a "zeroth approximation" for estimating the excess Gibbs energy of mixing: it must be emphasized that it is never exact and sometimes fails badly.

The aim of solubility parameter theory is to provide a self-consistent set of δ values for the various components at one temperature and pressure (usually 25°C, 1 atm). Because the enthalpy, excess entropy $S^E = -(\partial G^E/\partial T)_p$, and excess volume $V^E = (\partial G^E/\partial p)_T$ of mixing can be deduced from solubility parameter theory with even less success than that for excess Gibbs energy (section III.D), it is futile to attempt to calculate the temperature and pressure dependence of solubility parameters with any accuracy from these formal thermodynamic relations. Empirical relations may be used for this purpose (section VIII.B).

V. Evaluation of Solubility Parameters for Liquids

A. The One-Component Solubility Parameter

From eq 1 and 5 it is apparent that the main problem in evaluating δ is to obtain a value for the molar vaporization energy at the temperature required (frequently 25°C). If the enthalpy of vaporization has been determined calorimetrically at this temperature and if it is well below the boiling point, δ may be evaluated with the assumption that the vapor is ideal:

$$\delta = \left(\frac{\Delta_l^gH - RT}{V}\right)^{1/2} \tag{55}$$

At higher vapor pressures gas law corrections may be applied, but even at the normal boiling point the correction is usually quite small.[3,4]

Direct experimental information on Δ_l^gH is frequently unavailable, and several methods have been used to estimate it.[3,4,8,54,87,97] The diversity of these methods may be taken as indicating the fundamental nature of the solubility parameter, providing correlation between vaporization and critical, surface, and optical properties.

Despite the effort which has gone into the compilation of self-consistent sets of multiparameter solubility parameter, the simplicity of Burrell's original division of solvents into three classes has ensured its continuing popularity.[97] Consequently, the one-component solubility parameter, plus the hydrogen bonding group (poor, moderate, or strong), is still widely used for all types of solvents.

1. Variation of Vapor Pressure with Temperature

The Clausius–Clapeyron equation may be used:

$$\frac{d\ln p}{dT} = \frac{\Delta_l^gH}{pT\Delta_l^gV} \tag{56}$$

If it is assumed that the vapor is ideal, from eq 55 there is obtained

$$d\ln p/dT = \Delta_l^gH_{app}/RT^2 \tag{57}$$

which defines $\Delta_l^gH_{app}$, the apparent enthalpy of vaporization. In order to correct for nonideality, which is particularly important when the liquid molar volume is large, the compressibility factor

$$Z = pV_g/RT$$

is introduced[3]:

$$\delta = [(\Delta_l^gH_{app} - RT)Z/V]^{1/2}$$

Only values of p below about 10 kPa should be used to evaluate $\Delta_l^gH_t$, and $\Delta_l^gH_{25°C}$ is determined by interpolating or ex-

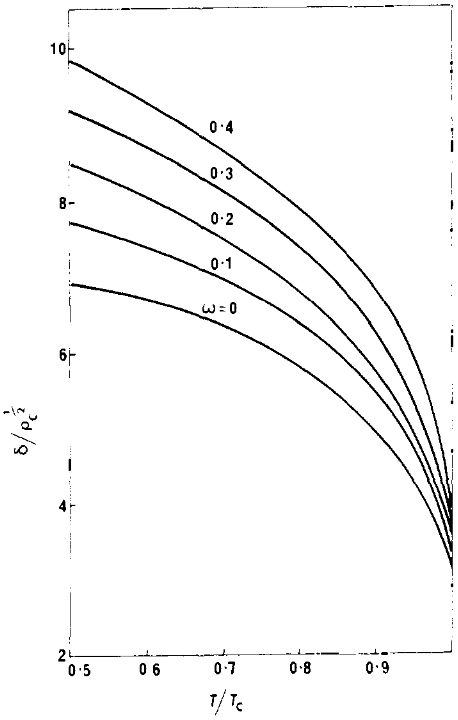

Figure 6. Reduced solubility parameter as a function of reduced temperature and acentric factor (after Lyckman, Eckert, and Prausnitz,[99] with the permission of *Chemical Engineering Science*).

trapolating.[4] (Tables of p–T relationships for common solvents are included in many chemical handbooks.)

Hoy[87] has used empirical vapor pressure relations in the determination of δ values for a wide range of liquids. For greater accuracy the Haggenmacher equation

$$\Delta_l{}^gH = \frac{dp}{dT}\frac{RT^2}{p}\frac{(1 - pT_c{}^3)^{1/2}}{p_cT^3} \tag{58}$$

(subscript c = critical), the Antoine equation

$$\log p = \frac{-B}{t + C} + A \tag{59}$$

and an exponential relation between $\Delta_l{}^gH$ and t were used (t = temperature in °C).

2. *Hildebrand's Empirical Equation*

A simple, convenient method is the application of Hildebrand's equation[4] in terms of the boiling point T_b:

$$\Delta_l{}^gH_{298K}/\text{J mol}^{-1} = -12{,}340 + 99.2T_b + 0.084T_b{}^2 \tag{60}$$

This is based on "Hildebrand's Rule" which states that the molar entropy of vaporization is the same for all regular liquids if measured at temperatures such that their vapors have equal volumes. Corrections should be made to the calculated values of δ in the case of hydrogen-bonded liquids:[97]

for alcohols, add 1.4 $\text{cal}^{1/2}\ \text{cm}^{-3/2}$ (2.9 $\text{MPa}^{1/2}$)
for esters, add 0.6 $\text{cal}^{1/2}\ \text{cm}^{-3/2}$ (1.2 $\text{MPa}^{1/2}$)
for ketones with bp < 100°C, add 0.5 $\text{cal}^{1/2}\ \text{cm}^{-3/2}$ (1.0 $\text{MPa}^{1/2}$)

3. *Corresponding States*

Molar volume, enthalpy of vaporization, and solubility parameter for nonpolar liquids have been expressed as empirical functions of the reduced temperature

$$T_r = T/T_c \tag{61}$$

and of other parameters.[98] This has been extended to larger molecules by using a quadratic function of the Pitzer acentric factor ω:

$$\delta/p_c{}^{1/2} = \delta_r{}^{(0)} + \omega\delta_r{}^{(1)} + \omega^2\delta_r{}^{(2)} \tag{62}$$

where $\delta_r{}^{(0)}$, $\delta_r{}^{(1)}$, and $\delta_r{}^{(2)}$ are empirically determined functions of T_r.[3,99,100] The generalized (reduced) solubility parameters are shown in Figure 6. A similar method has been applied to the properties of subcooled liquids for application to solid solubility in cryogenic solvents.[146]

4. *Structural Formulas*

The group contribution method (section IV.G and ref 101) may be applied to the estimation of δ. Care is necessary in the case of hydrogen-bonded liquids.

5. *Internal Pressure*

As discussed in section II.C, for van der Waals liquids

$$(\partial U/\partial V)_T = \Delta_l{}^gU/V$$

so from eq 2 and

$$T(\partial p/\partial T)_V = T\alpha/\kappa$$

it follows that

$$\delta \approx (T\alpha/\kappa)^{1/2} \tag{63}$$

The alternative approach of Bagley et al.[36] is to *define* δ in terms of the internal pressure.

6. *Viscosity Temperature Dependence*

The activation energy for viscous flow, E_η, has been found to be approximately proportional to the vaporization energy for both nonelectrolytes and ionic liquids (molten salts),[68] and this provides a useful scale for a broad range of solvents.[67]

7. *Other Empirical Relationships*

Rules have been developed[4,8,97] relating δ to van der Waals gas constant, surface tension, and refractive index.

B. The Dispersion Component

The dispersion component δ_d or λ may be determined from homomorph plots (section IV.F). Alternatively, Keller et al.[65] evaluated δ_d by means of correlation with the Lorentz–Lorenz refractive index (n) function for both nonpolar and slightly polar compounds. For $(n^2 - 1)/(n^2 + 2) = x \leqslant 0.28$ and $>$ 0.28, respectively,

$$\delta_d/\text{MPa}^{1/2} = 62.8x \text{ and }$$
$$-4.58 + 108x - 119x^2 + 45x^3 \tag{64}$$

The linear relation between δ_d and χ fails for values of χ greater than 0.28.

C. The Polar Component

In the work of Prausnitz et al.,[54,64] the polar component τ is obtained from eq 42 after E/V has been measured and λ estimated. Hansen and Skaarup[12] calculated the polar solubility parameter, using Böttcher's relation for estimating the contribution of the permanent dipoles to the cohesion energy of a fluid in terms of relative permittivity, refractive index, and dipole moment. This resulted in good correlation with the methods based on the homomorph concept and trial-and-error positioning of solvents in a three-dimensional system.

D. The Hydrogen-Bonding Component

Bondi and Simkin[84] showed that the enthalpies of vaporiza-

TABLE IV. Solvent Solubility Parameter Spectra (from Burrell[97])

	δ, cal$^{1/2}$ cm$^{-3/2}$	δ, MPa$^{1/2}$
Solvents Capable of Poor Hydrogen Bonding		
n-Pentane	7.0	14.3
n-Heptane	7.4	15.1
Methylcyclohexane	7.8	16.0
Solvesso 150	8.5	17.4
Toluene	8.9	18.2
Tetrahydronaphthalene	9.5	19.4
o-Dichlorobenzene	10.0	20.5
1-Bromonaphthalene	10.6	21.7
Nitroethane	11.1	22.7
Acetonitrile	11.8	24.1
Nitromethane	12.7	26.0
Solvents Capable of Moderate Hydrogen Bonding		
Diethyl ether	7.4	15.1
Diisobutyl ketone	7.8	16.0
n-Butyl acetate	8.5	17.4
Methylpropionate	8.9	18.2
Dibutyl phthalate	9.3	19.0
Dioxane	9.9	20.3
Dimethyl phthalate	10.7	21.9
2,3-Butylene carbonate	12.1	24.8
Propylene carbonate	13.3	27.2
Ethylene carbonate	14.7	30.1
Solvents Capable of Strong Hydrogen Bonding		
2-Ethylhexanol	9.5	19.4
Methylisobutylcarbinol	10.0	20.5
2-Ethylbutanol	10.5	21.5
1-Pentanol	10.9	22.3
1-Butanol	11.4	23.3
1-Propanol	11.9	24.3
Ethanol	12.7	26.0
Methanol	14.5	29.7

tion of alcohols could be predicted by considering them composed of a nonpolar contribution (calculated from data on the homomorph of the alcohol as discussed in section IV.F) and a hydrogen-bonding contribution which was considered independent of the molecular environment and determined by a set of rules from the molecular structure.

Hansen and Skaarup[12] calculated the hydrogen-bonding parameter δ_h (in cal$^{1/2}$ cm$^{-3/2}$) in an even simpler fashion, directly from $(5000N/V)^{1/2}$, where N is the number of alcohol groups in the molecule, V is the molar volume, and the figure 5000 arises from the fact that a reasonable value for the OH···O bond energy is 5000 cal mol^{-1}. The corresponding SI expression is

$$\delta_h = (20{,}900N/V)^{1/2}$$

The experimental origin of the spectroscopic hydrogen-bonding parameter γ introduced by Crowley et al.[63] has already been described (section IV.E).

The residual solubility parameter (eq 13) of Bagley et al.,[36] which was identified with the hydrogen-bonding parameter, may be evaluated from internal pressure, molar volume, and molar vaporization energy data, thus avoiding any use of the homomorph assumption.

Paruta[81] suggested an empirical relationship between δ and the relative permittivity ϵ which works best for hydrogen-bonded liquids:

$$\delta/\mathrm{MPa}^{1/2} = 0.45\epsilon + 18.5 \qquad (65)$$

Similar relations were used for other solvent classes.

E. Multicomponent Parameters

Hansen[9-12] used the techniques described above, as well as nearly 10,000 experimental observations of solubility and pigment suspension to provide a self-consistent set of δ_d, δ_p, and δ_h point values in a three-dimensional system. These data may be used with information on solute solubility volumes in three dimensions (section VI.B) to predict solvent-solute interaction behavior.

VI. Evaluation of Solubility Parameters for Nonvolatile Solutes

For nonvolatile solutes such as polymers it is not possible to determine δ values directly from $\Delta_l^g U$ as is done for liquids. A *solute* solubility parameter can be assumed to have exactly the same value as a *solvent* solubility parameter in the ideal case in which the solute and solvent mix in all proportions, without enthalpy or volume change, and without specific chemical interaction. More generally and practically, a variety of approaches is used.[8,97,102]

A. The One-Component Solubility Parameter

The Hildebrand or one-component solubility parameter may be determined by the following methods, the results of which have been discussed by Hildebrand and Scott.[4] The recent report on the determination of the cohesive energy of polytetrahydrofuran[103] illustrates the application of several techniques.

The one-parameter method is commonly used even when there are strong polar and hydrogen-bonding interactions. It has proved convenient to determine experimentally for commercial polymers a solubility parameter *range* for each hydrogen-bonded class (poor, moderate, strong) of solvent. The technique has been described by Burrell.[6,97]

1. Solvent Spectrum

A list of solvents can be compiled, with gradually increasing δ values (a "solvent spectrum": Table IV) such that the solute is soluble over a portion of the list.[97] The solute solubility parameter may then be taken approximately as the midpoint of the soluble range.

2. Polymer Swelling

The swelling of a slightly cross-linked analog of the polymer of interest in a series of solvents is studied, and the polymer is assigned the δ value of the liquid providing the maximum swelling coefficient. Either the swelling coefficient is plotted directly against solvent solubility parameter, or more accurately an expression incorporating the molar volume of each liquid may be used.[24,103,104] The effective solubility parameter of any proprietary composition material may be easily determined in this way; for example, inks can be chosen to avoid excessive swelling of applicator rollers.[7] A modification of this method is the gas chromatographic technique.[105]

3. Intrinsic Viscosity

The intrinsic viscosity of the solute is measured in a series of solvents, and the value of the solute solubility parameter is taken as equal to that of the solvent in which the solute intrinsic viscosity has a maximum value. As with the swelling method, allowance may also be made for the solvent molar volume.[103] Both equilibrium configuration of molecular chains in the swelling process and polymer solute viscosity depend on the balance between the Gibbs energy change due to mixing and that due to elastic deformation. The extent of deformation depends on the relative strengths of intramolecular (segment–segment) and intermolecular (segment–solvent) interactions.[24,93] In a good solvent the polymer molecule is unfolded, obtaining to the maximum extent the more favorable

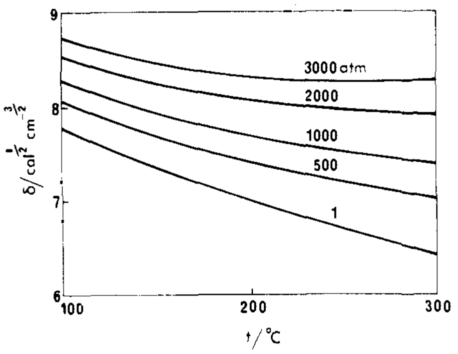

Figure 7. Calculated solubility parameter of liquid polyethylene (from Maloney and Prausnitz[32] with the permission of John Wiley and Sons, Inc.).

polymer–solvent interactions; in a poor solvent the molecule remains folded because of the more favorable intramolecular interactions.

4. *Molar Attraction Constants*

The assumption of additive molar attraction constants as the basis of an alternative approach was discussed in section IV.G. In this way information from the results of vapor pressure measurement on volatile compounds can be applied to nonvolatile polymers.[97]

5. *Temperature Dependence*

The solubility parameter of a polymer has been determined[106] from intrinsic viscosity measurements in a single solvent as a function of temperature by observation of the δ value for maximum intrinsic viscosity.

6. *Stress–Strain Behavior*

Polymer–solvent interaction parameters (χ), determined by stress–strain behavior or other physical property[56] of a swollen polymer may be related to δ values of solvent and polymer by[107]

$$\delta_A = \delta_B \pm [RT(\chi - \chi_S)/V_A]^{1/2} \qquad (66)$$

where V_A is the molar volume of the solvent and χ_S is the entropy contribution to χ. Plots of δ_A against $[RT(\chi - \chi_S)/V_A]^{1/2}$ are frequently linear,[56] yielding δ_B values from the intercept.

7. *Internal Pressure*

In the absence of hydrogen-bonding effects, the approach of Bagley and Chen (section IV.J) may be used to show that the "physical" solubility parameter can be evaluated from the internal pressure, which is determined as discussed in section V.A.5.

8. *Calculation*

An equation has been developed[108] for the calculation of the solubility parameter of a random copolymer from data available for the homopolymers. Thermodynamic properties, including solubility parameter, of molten polyethylene have been calculated by Maloney and Prausnitz[32] over a temperature and pressure range using limited experimental data and corresponding states correlations (Figure 7).

B. Multicomponent Parameters

Hansen[9-12] used a semiempirical method, based on the assumption that all the solvents for a polymer should be inside a certain $\delta_d - \delta_p - \delta_h$ volume, and all nonsolvents should be outside. The results of a large number of experimental observations were used in conjunction with a three-dimensional model for each polymer to divide the nondispersive solubility parameter into polar and hydrogen-bonding components. Projections of the solubility ellipsoid for poly(methyl methacrylate) are shown in Figure 8. For simplicity, the δ_d scale is usually expanded by a factor of 2, allowing a sphere to be drawn.

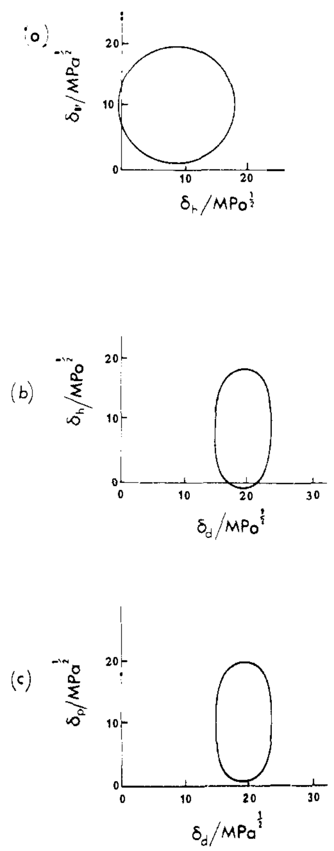

Figure 8. Projections of the solubility ellipsoid for poly(methyl methacrylate) on the (a) $\delta_p - \delta_h$, (b) $\delta_h - \delta_d$, and (c) $\delta_p - \delta_d$ planes. Expansion of the δ_d scale by a factor of 2 would yield circles. Liquids with solubility parameters lying within the solubility volume should be solvents for this polymer (after Hansen[21]).

VII. Data

A. Introductory Comment

The one-component solubility parameter originally defined by Hildebrand (eq 1) can be given a definite numerical value within the available experimental precision. As soon as multicomponent parameters such as δ_d, δ_p, δ_h (Hansen), δ, μ, γ (Crowley, et al.), λ, τ (Blanks and Prausnitz), or δ, γ (Lieberman, Cosaert) are used, the values become empirical and it is necessary to use a set of data which are self-consistent. If values are drawn from more than one source, inconsistencies arise, particularly when the homomorph concept is used.

If the promise of the two-component parameter of Bagley and coworkers (section IV.J) is fulfilled, this difficulty will be overcome: unambiguous values can be attributed to $\delta_V = \pi^{1/2}$ and to $\delta_r = (\Delta_l^gU - \pi V)^{1/2}V^{-1/2}$

B. Solvent Data

1. *One-Component Solubility Parameters Grouped According to Extent of Hydrogen-Bonding*

Burrell[97,102] has published extensive compilations of this information, listed both alphabetically by solvent and in order of increasing δ values. Shorter lists are included in other publica-

TABLE V. Solubility Parameter Values for Solvents, Including One-Component δ Values[a]

Name	H-bonding group	V, cm^3 mol^{-1}	δ, cal$^{1/2}$ cm$^{-3/2}$					δ, MPa$^{1/2}$				
			δ	δ_o	δ_d	δ_p	δ_h	δ	δ_o	δ_d	δ_p	δ_h
Alkanes												
n-Butane	P	101.4	6.8	6.9	6.9	0.0	0.0	13.9	14.1	14.1	0.0	0.0
n-Pentane	P	116.2	7.0	7.1	7.1	0.0	0.0	14.3	14.5	14.5	0.0	0.0
n-Hexane	P	131.6	7.3	7.3	7.3	0.0	0.0	14.9	14.9	14.9	0.0	0.0
n-Heptane	P	147.4	7.4	7.5	7.5	0.0	0.0	15.1	15.3	15.3	0.0	0.0
n-Octane	P	163.5	7.6	7.6	7.6	0.0	0.0	15.5	15.5	15.5	0.0	0.0
Dodecane	P	228.6	7.9	7.8	7.8	0.0	0.0	16.2	16.0	16.0	0.0	0.0
Cyclohexane	P	108.7	8.2	8.2	8.2	0.0	0.1	16.8	16.8	16.8	0.0	0.2
Methylcyclohexane	P	128.3	7.8	7.8	7.8	0.0	0.5	16.0	16.0	16.0	0.0	1.0
trans-Decahydronaphthalene (decalin)	P	156.9	8.8	8.8	8.8	0.0	0.0	18.0	18.0	18.0	0.0	0.0
Aromatic hydrocarbons												
Benzene	P	89.4	9.2	9.1	9.0	0.0	1.0	18.8	18.6	18.4	0.0	2.0
Toluene	P	106.8	8.9	8.9	8.8	0.7	1.0	18.2	18.2	18.0	1.4	2.0
Naphthalene[b]	P	111.5	9.9	9.9	9.4	1.0	2.9	20.3	20.3	19.2	2.0	5.9
Styrene	P	115.6	9.3	9.3	9.1	0.5	2.0	19.0	19.0	18.6	1.0	4.1
o-Xylene	P	121.2	8.8	8.8	8.7	0.5	1.5	18.0	18.0	17.8	1.0	3.1
Ethylbenzene	P	123.1	8.8	8.7	8.7	0.3	0.7	18.0	17.8	17.8	0.6	1.4
Mesitylene	P	139.8	8.8	8.8	8.8	0.0	0.3	18.0	18.0	18.0	0.0	0.6
Tetrahydronaphthalene	P	136.0	9.5	9.8	9.6	1.0	1.4	19.4	20.0	19.6	2.0	2.9
Halohydrocarbons												
Methyl chloride	M	55.4	9.7	8.3	7.5	3.0	1.9	19.8	17.0	15.3	6.1	3.9
Methyl dichloride	P	63.9	9.7	9.9	8.9	3.1	3.0	19.8	20.3	18.2	6.3	6.1
Chlorodifluoromethane (Freon 21)	P	72.9	8.3	7.3	6.0	3.1	2.8	17.0	14.9	12.3	6.3	5.7
Ethyl bromide	M	76.9	9.6	8.3	7.7	1.5	2.8	19.6	17.0	15.8	3.1	5.7
1,1-Dichloroethylene	P	79.0	9.1	9.2	8.3	3.3	2.2	18.6	18.8	17.0	6.8	4.5
Ethylene dichloride	P	79.4	9.8	10.2	9.3	3.6	2.0	20.0	20.9	19.0	7.4	4.1
Methylene diiodide	M	80.5	10.2	9.3[c]	8.7[c]	1.9[c]	2.7[c]	20.9	19.0[c]	17.8[c]	3.9[c]	5.5[c]
Chloroform	P	80.7	9.3	9.3	8.7	1.5	2.8	19.0	19.0	17.8	3.1	5.7
Ethylene dibromide	P	87.0	9.7	11.7	9.6	3.3	5.9	19.8	23.9	19.6	6.8	12.1
n-Propyl chloride	M	88.1	8.5	8.7	7.8	3.8	1.0	17.4	17.8	16.0	7.8	2.0
Trichloroethylene	P	90.2	9.2	9.3	8.8	1.5	2.6	18.8	19.0	18.0	3.1	5.3
Dichlorodifluoromethane (Freon 12)	P	92.3	5.5	6.1	6.0	1.0	0.0	11.3	12.5	12.3	2.0	0.0
Carbon tetrachloride	P	97.1	8.6	8.7	8.7	0.0	0.3	17.6	17.8	17.8	0.0	0.6
Tetrachloroethylene (perchloroethylene)	P	101.1	9.3	9.9	9.3	3.2	1.4	19.0	20.3	19.0	6.5	2.9
Chlorobenzene	P	102.1	9.5	9.6	9.3	2.1	1.0	19.4	19.6	19.0	4.3	2.0
1,1,2,2-Tetrachloroethane	P	105.2	9.7	10.6	9.2	2.5	4.6	19.8	21.7	18.8	5.1	9.4
Bromobenzene	P	105.3	9.9	10.6	10.0	2.7	2.0	20.3	21.7	20.5	5.5	4.1
o-Dichlorobenzene	P	112.8	10.0	10.0	9.4	3.1	1.6	20.5	20.5	19.2	6.3	3.3
1,1,2-Trichlorotrifluoroethane (Freon 113)	P	119.2	7.3	7.2	7.2	0.8	0.0	14.9	14.7	14.7	1.6	0.0
1-Bromonaphthalene	P	140.0	10.6	10.2	9.9	1.5	2.0	21.7	20.9	20.3	3.1	4.1
Ethers												
Furan	M	72.5	9.4	9.1	8.7	0.9	2.6	19.2	18.6	17.8	1.8	5.3
Epichlorohydrin	S	79.9	11.0	10.7	9.3	5.0	1.8	22.5	21.9	19.0	10.2	3.7
Tetrahydrofuran	M	81.7	9.1	9.5	8.2	2.8	3.9	18.6	19.4	16.8	5.7	8.0
1,4-Dioxane	M	85.7	10.0	10.0	9.3	0.9	3.6	20.5	20.5	19.0	1.8	7.4
Diethyl ether	M	104.8	7.4	7.7	7.1	1.4	2.5	15.1	15.8	14.5	2.9	5.1
Ketones												
Acetone	M	74.0	9.9	9.8	7.6	5.1	3.4	20.3	20.0	15.5	10.4	7.0
Methyl ethyl ketone	M	90.1	9.3	9.3	7.8	4.4	2.5	19.0	19.0	16.0	9.0	5.1
Cyclohexanone	M	104.0	9.9	9.6	8.7	3.1	2.5	20.3	19.6	17.8	6.3	5.1
Diethyl ketone	M	106.4	8.8	8.9	7.7	3.7	2.3	18.0	18.1	15.8	7.6	4.7
Mesityl oxide	M	115.6	9.0	9.2	8.0	3.5	3.0	18.4	18.9	16.4	6.1	6.1
Acetophenone	M	117.4	10.6	10.6	9.6	4.2	1.8	21.8	21.8	19.6	8.6	3.7
Methyl isobutyl ketone	M	125.8	8.4	8.3	7.5	3.0	2.0	17.2	17.0	15.3	6.1	4.1
Methyl isoamyl ketone	M	142.8	8.4	8.5	7.8	2.8	2.0	17.2	17.4	16.0	5.7	4.1
Isophorone	M	150.5	9.1	9.7	8.1	4.0	3.6	18.6	19.9	16.6	8.2	7.4
Di(isobutyl) ketone	M	177.1	7.8	8.3	7.8	1.8	2.0	16.0	16.9	16.0	3.7	4.1
Aldehydes												
Acetaldehyde	M	57.1	10.3	9.9[c]	7.2[c]	3.9[c]	5.5[c]	21.1	20.2[c]	14.7[c]	8.0[c]	11.3[c]
Furfural	M	83.2	11.2	11.9	9.1	7.3	2.5	22.9	24.4	18.6	14.9	5.1
Butyraldehyde	M	88.5	9.0	8.4	7.2	2.6	3.4	18.4	17.1	14.7	5.3	7.0
Benzaldehyde	M	101.5	9.4	10.5	9.5	3.6	2.6	19.2	21.5	19.4	7.4	5.3

TABLE V (*Continued*)

Name	H-bonding group	V, cm^3 mol^{-1}	δ, cal$^{1/2}$ cm$^{-3/2}$					δ, MPa$^{1/2}$				
			δ	δ_o	δ_d	δ_p	δ_h	δ	δ_o	δ_d	δ_p	δ_h
Esters												
Ethylene carbonate	M	66.0	14.7	14.5	9.5	10.6	2.5	30.1	29.6	19.4	21.7	5.1
γ-Butyrolactone	M	76.8	12.6	12.9	9.3	8.1	3.6	25.8	26.3	19.0	16.6	7.4
Methyl acetate	M	79.7	9.6	9.2	7.6	3.5	3.7	19.6	18.7	15.5	7.2	7.6
Ethyl formate	M	80.2	9.4	9.6	7.6	4.1	4.1	19.2	19.6	15.5	8.4	8.4
Propylene-1,2 carbonate	M	85.0	13.3	13.3	9.8	8.8	2.0	27.2	27.3	20.0	18.0	4.1
Ethyl acetate	M	98.5	9.1	8.9	7.7	2.6	3.5	18.6	18.1	15.8	5.3	7.2
Diethyl carbonate	M	121	8.8	8.8	8.1	1.5	3.0	18.0	17.9	16.6	3.1	6.1
n-Butyl acetate	M	132.5	8.5	8.5	7.7	1.8	3.1	17.4	17.4	15.8	3.7	6.3
Isobutyl acetate	M	133.5	8.3	8.2	7.4	1.8	3.1	17.0	16.8	15.1	3.7	6.3
Isoamyl acetate	M	148.8	7.8	8.4	7.5	1.5	3.4	16.0	17.1	15.3	3.1	7.0
Dimethyl phthalate	M	163.0	10.7	10.8	9.1	5.3	2.4	21.9	22.1	18.6	10.8	4.9
Diethyl phthalate	M	198	10.0	10.0	8.6	4.7	2.2	20.5	20.6	17.6	9.6	4.5
Di-*n*-butyl phthalate	M	266	9.3	9.9	8.7	4.2	2.0	19.0	20.2	17.8	8.6	4.1
Tricresyl phosphate	M	316	8.4	11.3	9.3	6.0	2.2	17.2	23.1	19.0	12.3	4.5
Dioctyl phthalate	M	377	7.9	8.9	8.1	3.4	1.5	16.2	18.2	16.6	7.0	3.1
Nitrogen compounds												
Acetonitrile	P	52.6	11.9	12.0	7.5	8.8	3.0	24.3	24.4	15.3	18.0	6.1
Acrylonitrile	P	67.1	10.5	12.1	8.0	8.5	3.3	21.5	24.8	16.4	17.4	6.8
Propionitrile	P	70.9	10.8	10.6	7.5	7.0	2.7	22.1	21.7	15.3	14.3	5.5
Benzonitrile	P	102.6	8.4	9.7	8.5	4.4	1.6	17.2	19.9	17.4	9.0	3.3
Nitromethane	P	54.3	12.7	12.3	7.7	9.2	2.5	26.0	25.1	15.8	18.8	5.1
Nitroethane	P	71.5	11.1	11.1	7.8	7.6	2.2	22.7	22.7	16.0	15.5	4.5
2-Nitropropane	P	86.9	9.9	10.1	7.9	5.9	2.0	20.3	20.6	16.2	12.1	4.1
Nitrobenzene	P	102.7	10.0	10.9	9.8	4.2	2.0	20.5	22.2	20.0	8.6	4.1
Ethylenediamine	S	67.3	12.3	12.4	8.1	4.3	8.3	25.2	25.3	16.6	8.8	17.0
2-Pyrrolidone	S	76.4	14.7	13.9	9.5	8.5	5.5	30.1	28.4	19.4	17.4	11.3
Pyridine	S	80.9	10.7	10.7	9.3	4.3	2.9	21.9	21.8	19.0	8.8	5.9
Morpholine	S	87.1	10.8	10.5	9.2	2.4	4.5	22.1	21.5	18.8	4.9	9.2
Aniline	S	91.5	10.3	11.0	9.5	2.5	5.0	21.1	22.6	19.4	5.1	10.2
N-Methyl-2-pyrrolidone	M	96.5	11.3	11.2	8.8	6.0	3.5	23.1	22.9	18.0	12.3	7.2
n-Butylamine	S	99.0	8.7	9.1	7.9	2.2	3.9	17.8	18.6	16.2	4.5	8.0
Diethylamine	S	103.2	8.0	8.0	7.3	1.1	3.0	16.4	16.3	14.9	2.3	6.1
Quinoline	S	118.0	10.8	10.8	9.5	3.4	3.7	22.1	22.0	19.4	7.0	7.6
Formamide	S	39.8	19.2	17.9	8.4	12.8	9.3	39.3	36.6	17.2	26.2	19.0
Dimethylformamide	M	77.0	12.1	12.1	8.5	6.7	5.5	24.8	24.8	17.4	13.7	11.3
N,*N*-Dimethylacetamide	M	92.5	10.8	11.1	8.2	5.6	5.0	22.1	22.7	16.8	11.5	10.2
Hexamethylphosphoramide	S	175.7	10.5	11.4	9.0	4.2	5.5	21.5	23.2	23.2	8.6	11.3
Sulfur compounds												
Carbon disulfide	P	60.0	10.0	10.0	10.0	0.0	0.3	20.5	20.5	20.5	0.0	0.6
Dimethyl sulfoxide	M	71.3	12.0	13.0	9.0	8.0	5.0	24.5	26.7	18.4	16.4	10.2
Dimethyl sulfone^b	M	75	14.5	14.6	9.3	9.5	6.0	29.7	29.8	19.0	19.4	12.3
Acid halides and anhydrides												
Acetyl chloride	M	71.0	9.5	9.5	7.7	5.2	1.9	19.4	19.4	15.8	10.6	3.9
Succinic anhydride^b	S	66.8	15.4	15.4	9.1	9.4	8.1	31.5	31.5	18.6	19.2	16.6
Acetic anhydride	S	94.5	10.3	10.9	7.8	5.7	5.0	21.1	22.3	16.0	11.7	10.2
Monohydric alcohols												
Methanol	S	40.7	14.5	14.5	7.4	6.0	10.9	29.7	29.6	15.1	12.3	22.3
Ethanol	S	58.5	12.7	13.0	7.7	4.3	9.5	26.0	26.5	15.8	8.8	19.4
Ethylene cyanohydrin (hydracrylonitrile)	S	68.3	15.2	15.1	8.4	9.2	8.6	31.1	31.0	17.2	18.8	17.6
Allyl alcohol	S	68.4	11.8	12.6^c	7.9^c	5.3^c	8.2^c	24.1	25.7^c	16.2^c	10.8^c	16.8^c
1-Propanol	S	75.2	11.9	12.0	7.8	3.3	8.5	24.3	24.5	16.0	6.8	17.4
2-Propanol	S	76.8	11.5	11.5	7.7	3.0	8.0	23.5	23.5	15.8	6.1	16.4
Furfuryl alchol	S	86.5	12.5	11.9	8.5	3.7	7.4	25.6	24.3	17.4	7.6	15.1
1-Butanol	S	91.5	11.4	11.3	7.8	2.8	7.7	23.3	23.1	16.0	5.7	15.8
2-Butanol	S	92.0	10.8	10.8	7.7	2.8	7.1	22.1	22.2	15.8	5.7	14.5
Benzyl alchol	S	103.6	12.1	11.6	9.0	3.1	6.7	24.8	23.8	18.4	6.3	13.7
Cyclohexanol	S	106.0	11.4	11.0	8.5	2.0	6.6	23.3	22.4	17.4	4.1	13.5
2-Ethyl-1-butanol	S	123.2	10.5	10.4	7.7	2.1	6.6	21.5	21.2	15.8	4.3	13.5
Diacetone alcohol	M	124.2	9.2	10.2	7.7	4.0	5.3	18.8	20.8	15.8	8.2	10.8
Ethyl lactate	M	115	10.0	10.6	7.8	3.7	6.1	20.5	21.6	16.0	7.6	12.5
n-Butyl lactate	M	149	9.4	9.7	7.7	3.2	5.0	19.2	19.9	15.8	6.5	10.2
Ethylene glycol monomethyl ether	M	79.1	11.4	12.1	7.9	4.5	8.0	23.3	24.8	16.2	9.2	16.4
Ethylene glycol monoethyl ether	M	97.8	10.5	11.5	7.9	4.5	7.0	21.5	23.5	16.2	9.2	14.3

TABLE V (*Continued*)

Name	H-bonding group	V, cm^3 mol^{-1}	δ, cal$^{1/2}$ cm$^{-3/2}$					δ, MPa$^{1/2}$				
			δ	δ_o	δ_d	δ_p	δ_h	δ	δ_o	δ_d	δ_p	δ_h
Diethylene glycol monomethyl ether	M	130.9	8.5	10.9	7.9	4.5	6.0	17.4	22.3	16.2	9.2	12.3
Ethylene glycol mono-*n*-butyl ether	M	131.6	9.5	10.2	7.8	2.5	6.0	19.4	20.8	16.0	5.1	12.3
2-Ethyl-1-hexanol	S	157.0	9.5	9.9	7.8	1.6	5.8	19.4	20.2	16.0	3.3	11.9
1-Octanol	S	157.7	10.3	10.3	8.3	1.6	5.8	21.1	21.0	17.0	3.3	11.9
Diethylene glycol mono-*n*-butyl ether	S	170.6	12.1	10.0	7.8	3.4	5.2	24.8	20.4	16.0	7.0	10.6
Carboxylic acids												
Formic acid	S	37.8	12.1	12.2	7.0	5.8	8.1	24.8	24.9	14.3	11.9	16.6
Acetic acid	S	57.1	10.1	10.5	7.1	3.9	6.6	20.7	21.4	14.5	8.0	13.5
n-Butyric acid	S	110	10.5	9.2^c	7.3^c	2.0^c	5.2^c	21.5	18.8^c	14.9^c	4.1^c	10.6^c
Phenols												
m-Cresol	S	104.7	10.2	11.1	8.8	2.5	6.3	20.9	22.7	18.0	5.1	12.9
Methyl salicylate	M	129	10.6	10.6	7.8	3.9	6.0	21.7	21.7	16.0	8.0	12.3
Polyhydric alcohols												
Ethylene glycol	S	55.8	14.6	16.1	8.3	5.4	12.7	29.9	32.9	17.0	11.0	26.0
Glycerol	S	73.3	16.5	17.7	8.5	5.9	14.3	33.8	36.1	17.4	12.1	29.3
Propylene glycol	S	73.6	12.6	14.8	8.2	4.6	11.4	25.8	30.2	16.8	9.4	23.3
1,3-Butanediol	S	89.9	11.6	14.1	8.1	4.9	10.5	23.7	28.9	16.6	10.0	21.5
Diethylene glycol	S	95.3	12.1	14.6	7.9	7.2	10.0	24.8	29.9	16.2	14.7	20.5
Triethylene glycol	S	114.0	10.7	13.5	7.8	6.1	9.1	21.9	27.5	16.0	12.5	18.6
Water	S	18.0	23.4^c	23.4^c	7.6^c	7.8^c	20.7^c	47.9	47.8^c	15.5^c	16.0^c	42.3^c

[a] Classification as strongly (S), moderately (M), or poorly (P) hydrogen-bonding (selected from Burrell[97]); and dispersive (d), polar (p), hydrogen-bonding (h), and total (0) 25°C solubility parameters and molar volumes (selected from Hansen and Beerbower[22]). [b] Solid at 25°C, but treated as subcooled liquid. [c] Value uncertain.

TABLE VI. Approximate Solubility Parameter Ranges for Some Solutes in Solvents Which Are Poorly (P), Moderately (M), or Strongly (S) Hydrogen Bonded

Name	δ, cal$^{1/2}$ cm$^{-3/2}$			δ, MPa$^{1/2}$		
	δ_P	δ_M	δ_S	δ_P	δ_M	δ_S
Butadiene–acrylonitrile copolymer (Buna N)	8.7–9.3			17.8–19.0		
Cellulose			14.5–16.5			29.7–33.8
Cellulose acetate	11.1–12.5	10.0–14.5		22.7–25.6	20.5–29.7	
Epoxy (Epon 1001)	10.6–11.1	8.5–13.3		21.7–22.7	17.4–27.2	
Hexa(methoxymethyl)-melamine	8.5–11.8	8.5–14.7	9.5–16.5	17.4–24.1	17.4–30.1	19.4–33.8
Nitrocellulose	11.1–12.5	8.0–14.5	12.5–14.5	22.7–25.6	16.4–29.7	25.6–29.7
Phenolic resins	8.5–11.5	7.8–13.2	9.5–13.6	17.4–23.5	16.0–27.0	19.4–27.8
Polyacrylonitrile		12.0–14.0			24.5–28.6	
Polycarbonate	9.5–10.6	9.5–10.0		19.4–21.7	19.4–20.5	
Polyethylene	7.7–8.2			15.8–16.8		
Poly(ethylene oxide) (Carbowax 4000)	8.9–12.7	8.5–14.5	9.5–14.5	18.2–26.0	17.4–29.7	19.4–29.7
Poly(ethylene phthalate) (Mylar)	9.5–10.8	9.3–9.9		19.4–22.1	19.0–20.3	
Poly(hexamethylene adipamide)(Nylon Type 8)			11.9–14.5			24.3–29.7
Poly(methyl methacrylate)	8.9–12.7	8.5–13.3		18.2–26.0	17.4–27.2	
Polystyrene	8.5–10.6	9.1–9.4		17.4–21.7	18.6–19.2	
Polytetrafluoroethylene	5.8–6.4			11.9–13.1		
Polyurethane	9.8–10.3			20.0–21.1		
Poly(vinyl acetate)	8.5–9.5			17.4–19.4		
Poly(vinyl chloride)	8.5–11.0	7.8–10.5		17.4–22.5	16.0–21.5	
Rubber (natural)	8.1–8.5			16.6–17.4		
Rubber (chlorinated)	8.5–10.6	7.8–10.8		17.4–21.7	16.0–22.1	
Shellac		10.0–11.0	9.5–14.0		20.5–22.5	19.4–28.6
Silicone (DC-1107)	7.0–9.5	9.3–10.8	9.5–11.5	14.3–19.4	19.0–22.1	19.4–23.5

tions by Burrell,[8] Sheehan and Bisio,[56] and Seymour.[109,110] Table V contains δ values for selected solvents.

2. *Multicomponent Solubility Parameters*

Hansen's publications[9,10,12,14,22] include lists of his three-component solubility parameters, with modifications from time to time to improve self-consistency. The review by Hansen and Beerbower[22] has the most complete list of recent values, and a selection of these is included in Table V. Burrell has included Hansen's values in the second edition of "Polymer Handbook".[97] Hoy[87,111] has provided very extensive lists, which although precise and self-consistent, sometimes differ from previously reported values which have been used as the basis of polymer solubility parameter ranges.[18] Care should be exercised in using solvent and solute parameters from different sources.

Authors of other multicomponent schemes have also published lists of values.

Crowley et al.[63,89]: solubility parameter, dipole moment, hydrogen bonding parameter;

Gardon,[20,55] Teas,[91] and Vial[92,93]: solubility parameters and fractional polarities.

Lieberman[74] and Cosaert[19]: solubility parameter and hydrogen bonding parameter.

Nelson et al.[90]: solubility parameter, fractional polarity, and net hydrogen bonding index.

Columns "δ" and "δ_0" in Table V provide a comparison of the results of one-component and three-component approaches to solubility parameter determinations. Significant disparity in these values for a liquid indicates the existence of particular interactions or features not explained by the current approach. Fluorocarbons form one class of liquids with such a problem (section VIII.B), and this is demonstrated particularly in fluorocarbon–hydrocarbon mixtures.

C. Data for Polymers and Other Solutes

1. *One-Component Solubility Parameter Ranges Grouped According to Solvent Hydrogen-Bonding Type*

The main compilations are those of Burrell[17,97,102] and Gordon,[20] and other lists have been published by Burrell[8,112] and Seymour.[109,110] Table VI contains ranges for selected solutes.

2. *Multicomponent Solubility Parameters*

Hansen[9,14,21] has determined regions or volumes of solubility in his three-component system for a variety of polymers. In addition, most of the authors listed at the end of section VII.B.2 have included information on the positions occupied by various solutes in their particular solubility parameter schemes, but there are no extensive compilations. Sandholm[24] has published a short bibliography of polymer solubility data.

VIII. Other Factors in the Use of Solubility Parameters

A. Other Tests of Solvent Power

1. *Dilution Ratios*

Dilution ratio (ASTM Method D1720-62) is used to express the tolerance of solvents to diluents, particularly toluene. The multiparameter approach provides a satisfactory correlation with solubility parameters[63] although the one-component solubility parameter is not able to do this.[6] The dilution ratio technique was in fact used to determine the exact position of the "gel" region between the soluble and nonsoluble zones of solute behavior.[63]

TABLE VII. Calculated Variation of Solubility Parameters with Temperature for Two Liquids (after Hansen and Beerbower[22])

	$d\delta/dT$, cal$^{1/2}$ cm$^{-3/2}$ K^{-1}			$d\delta/dT$, MPa$^{1/2}$ K^{-1}		
	$d\delta_d/dT$	$d\delta_p/dT$	$d\delta_h/dT$	$d\delta_d/dT$	$d\delta_p/dT$	$d\delta_h/dT$
Acetone	−11.1	−3.0	−6.1	−22.7	−6.1	−12.5
1-Propanol	−9.3	−1.6	−14.5	−19.0	−3.3	−29.7

2. *Kauri-Butanol Test*

Another commonly used measure of the solvent power of liquids is their Kauri-Butanol (KB) value, obtained by titrating a standard Kauri resin solution (20 wt % in 1-butanol: ASTM Method D1133-54T) with the solvent until a cloud point is reached. Although KB values have been related to solubility parameter by functions such as[6,97,113]

$$\delta/\text{MPa}^{1/2} = 12.9 + 0.06(\text{KB}) \tag{67}$$

the KB value is in fact primarily a measure of the aromaticity of solvents.[109]

B. Effect of Temperature, Pressure, and Volume on Solubility Parameters

For hydrocarbon solvents the average decrease in δ for each 1°C *temperature* rise is ~0.01, which for many practical purposes has little effect. In addition, the values of $V_B\phi_A{}^2(\delta_A - \delta_B)^2$ and $V_A\phi_B{}^2(\delta_A - \delta_B)^2$ are nearly independent of temperature because of the similar effect of temperature on δ_A and δ_B, so the entropy–temperature factor (see eq 32 and 38) is usually far more important.[8,22,47]

If precise information is required on the temperature dependence of the dispersion component δ_d, empirical functions may be used[4,87] (see section V.A.1 for the temperature dependence of $\Delta_l{}^gH$). Hansen and Beerbower[22] have reviewed methods of calculating the variation with temperature of δ_d, δ_p, and δ_h, and their results are summarized in Table VII. The effect on a solvent solubility parameter of changing temperature has been utilized[106] to provide a solubility parameter spectrum for determination of a polymer solubility parameter.

The effect of molar *volume* also appears in the entropy term as well as in the solubility parameter term. Thus for an extraction solvent (see section X.B) when the Flory–Huggins entropy correction for dissimilar volumes is included (eq 76) V_B appears in almost every term for the activity coefficient, and the selectivity of an extraction solvent depends both on solubility parameter components and on the molar volumes.[22] All other factors being equal, the solvent with the lower molar volume is superior thermodynamically, but the effect of molar volume usually has been neglected, partly because molar volumes of common solvents are rather similar and partly to reduce the number of parameters for simplicity. It is particularly significant in the case of aliphatic hydrocarbons, with similar δ values and different molar volumes.[113] Fluorocarbons, with larger volumes, have smaller solubility parameters than the corresponding hydrocarbons.[62]

The most significant effect of large increases in *pressure* is the decrease in volume, i.e., equivalent to reductions in temperature. The effect of pressure has received little attention, although high-pressure gas chromatography (section VIII.G) makes use of the solubility parameter for supercritical fluids.

The effect of pressure and temperature on solubility in marginal situations can be important.[114] An example of the way solubility parameters may be calculated as a function of temperature (100–300°C) and pressure (1–3000 atm) is the work on polythene of Maloney and Prausnitz[32] (Figure 7).

C. Effect of Concentration

Burrell[7] has emphasized the importance of concentration dependence in situations where there is a disparity in δ values (greater than about 2.3 MPa$^{1/2}$). From eq 35 it can be seen that the heat of mixing per unit volume has a maximum value when both ϕ_A and ϕ_B are 0.5, that is, when equal volumes of the components are mixed, but when there is a close match in δ values the Gibbs energy is negative at all concentrations. There are concentration inconsistencies in the various experimental methods used to determine solubility parameters; the current approach is to adjust the concentration to correspond to commercial usage. A practical problem is that a solvent system which is suitable at high solute concentration may produce insolubility at dilute concentrations, for example, during clean-up operations.

D. Mixed Solvents

Practical solvents are usually blends, and it is therefore important to be able to evaluate the effective solubility parameter of a solvent mixture. Other factors such as viscosity, volatility, and cost must be considered in solvent formulation (section VIII.F), but the effective solubility parameter is of great importance.

In solubility parameter theory[3] the $\bar{\delta}$ value for a solvent mixture where all components have a similar molar volume is related to the volume fraction ϕ_i and solubility parameter δ_i of the components by the expression

$$\bar{\bar{\delta}} = \sum_i \phi_i\delta_i \tag{68}$$

where the summation extends over all components, including the solute where its volume fraction is appreciable.

Equation 68, predicting that the value of the solubility parameter for a solvent mixture is volume-wise proportional to the solubility parameters of the components is by no means quantitatively accurate[115] but has been used widely with reasonable success (ref 6, 55, 63, 90, 116; see section VIII.F). It is certainly true in general terms that the addition of a nonsolvent may improve the solubility of a solute in a solvent, and even that a solute may be soluble in a mixture of two nonsolvents, for example,[8] ether (δ = 15.1 MPa$^{1/2}$)–ethanol (δ = 26.0 MPa$^{1/2}$) as a solvent mixture for nitrocellulose (δ = 23 MPa$^{1/2}$).

Purkayastha and Walkley[115] have attempted to improve on eq 68 by defining an "effective volume fraction", ϕ^*. For the solute B in an (A + C) solvent mixture ($\phi_A + \phi_C \approx 1$)

$$\delta_{A-C} = \phi_A{}^*\delta_A + \phi_C{}^*\delta_C \tag{69}$$

and

$$\frac{\phi_A{}^*}{\phi_C{}^*} = \frac{\phi_A(\delta_B - \delta_C)^2}{\phi_C(\delta_B - \delta_A)^2} \tag{70}$$

That is, the effective volume fraction terms are related to the bulk volume fraction terms by the inverse of the heats of mixing of the solute B in each of the pure solvents A and C. This has the disadvantage that the behavior in the limit $(\delta_B - \delta_A) \rightarrow 0$, $(\delta_B - \delta_C) \rightarrow 0$ is unclear.

E. Solvent Formulation

Solubility is not the only criterion in blending solvents. The formulation of a solvent blend for any purpose is governed by volatility (relative evaporation rate), photochemical air pollution regulations (e.g., the Los Angeles County Rule 66), toxicity, viscosity, flammability, cost, and availability.[14,113,117] These factors are usually used for initial solvent selection, and this is followed by solubility parameter optimization, using one of the methods of section IV. Application of eq 68 is usually adequate for the determination of the average solubility parameter for a blend.

Graphical techniques are adequate for a two-component parameter system, but require more effort in the three-component methods.[9,19] Although computer-programmed methods have been used for this purpose,[90,118] some workers consider them unnecessary.[14]

F. Polymer Crystallinity

For completely amorphous polymers there is no enthalpy change on fusion, but when crystalline polymers dissolve, the overall enthalpy change must also provide energy to melt the crystallites, the fusion entropy requirement outweighing the entropy change caused by the disordering process. Highly crystalline polymers (e.g., polyethylene, polypropylene, polytetrafluoroethylene) well below their melting points are insoluble in all solvents. While the solubility parameter is extremely useful for predicting the solubility behavior of amorphous polymers, crystalline polymers pose one of the challenges for the solubility parameter method.[7]

G. Solubility Parameters of Compressed Gases and Subcooled Liquid

In their review of high-pressure gas chromatography for nonvolatile species, Giddings, et al.[119] extended the use of the one-component solubility parameter to gases at liquid density. Their assumption of a "state effect" related to the reduced density ratio of vapor and liquid and a "chemical effect" related to the critical pressure (compare eq 62) led them to the expression

$$\delta/\text{cal}^{1/2}\ \text{cm}^{-3/2} = 1.25(p_c{}^{1/2}/\text{atm}^{1/2})\,(\rho_r{}^g/\rho_r{}^l) \tag{71}$$

It has already been noted (section V.A.3) that Prausnitz and coworkers[146] have developed a method to determine the reduced solubility parameters of subcooled liquids. Table V includes the solubility parameters of some solids obtained by treating them as subcooled liquids.[22] Further developments are to be expected in this area with the increasing use of high-pressure and low-temperature techniques. A related subject is gas–liquid solubility (section X.C).

IX. Surface Properties and Pigment Dispersion

A. Relation between Liquid Surface Free Energies and Solubility Parameters

Following the empirical relationship of Hildebrand[4] and the theoretical but idealized treatment of Schonhorn,[120] Beerbower[121] provided a correlation on a three-component solubility parameter basis for most organic liquids

$$\gamma = 0.0715\,V^{1/2}[\delta_d{}^2 + 0.632(\delta_p{}^2 + \delta_h{}^2)] \tag{72}$$

for the surface free energy γ in ergs cm^{-2} (1 erg cm^{-2} = 10^{-3} N m^{-1}), molar volume V in mol cm^{-3}, and δ values in cal$^{1/2}$ cm$^{-3/2}$. Similar relations hold for liquid metals and several classes of molten salts. Work on solvent blends has been reviewed by Hansen and Beerbower.[22]

Considering the general, universal importance of the cohesive energy density in all physical properties, it is not surprising that such relationships can be found, but their detailed significance should not be overemphasized. In practical applications of coatings, chromatography, etc., the problem is much more complicated than the simple solvent–air or solvent–vapor situation as it involves in addition organic polymer–inorganic crystal and organic polymer–solvent interfaces. This poses another challenge for solubility parameter theory.[7]

B. Liquid–Solid Interactions

Adsorption on a solid surface from the gas phase in principle can be described by obtaining solubility parameters for the adsorbent surface from suitable experimental data—an extension of the solvent spectrum method (section VI.A). Gas chromatography was studied in this way by Vial.[93] It should be noted that it is the surface, not the bulk of the material which is thus characterized, and surface properties may vary between apparently identical bulk samples.

Adsorption from solution involves additional solute–solvent and adsorbent–solvent interactions, but in some cases these can cancel.[65,122] Little progress has been made in this direction, and it is questionable how much further effort is justified considering how far removed this situation is from that of a regular solution.

The subject has been reviewed briefly by Hansen and Beerbower[22] who reported the work of Zisman,[123] Wu,[124] and Hansen.[125] Hansen[125] has described the characterization of a variety of solid surfaces (polymers and tin-plate) in terms of three-component solubility parameters.

C. Liquid–Solid Chromatography

The relative extent of solute adsorption from different solvents may be described by the solvent strength parameter ϵ^0. As is the case with the solubility parameter, the solvent strength parameter may be treated either as an empirical parameter or as a fundamental property theoretically related to adsorption energies.[122] Recently there has been interest in the degree of correlation between liquid solubility parameter and liquid–solid solvent strength parameter.[65,119,126] In qualitative terms, the eluotropic series of increasing elution strengths of various liquids closely follows the order of one-component solubility parameters, and this is attributable to the fact that both δ and ϵ^0 reflect the ability of a solvent molecule to form physico-chemical bonds with an adjacent molecule. Good quantitative agreement would not be expected. Solvent strength is based on four types of interaction: (i) solute–adsorbent, (ii) solvent–adsorbent, (iii) solvent–solvent, and (iv) solute–solvent, of which the first two are predominant. The solubility parameter measures only the third and fourth types. The approximate empirical relationships[126] for δ in cal$^{1/2}$ cm$^{-3/2}$

$$\epsilon^0(\text{alumina}) = -0.786 + 0.125\delta$$
$$\epsilon^0(\text{silica}) = -0.519 + 0.088\delta \qquad (73)$$

have linear regression coefficients of 0.813 or 66.1% dependence of ϵ^0 on δ. For mixed solvents, quantitative ϵ^0–δ correlations are even less reliable.

D. Pigment Dispersion

Despite the practical importance of pigment dispersion, relatively little fundamental work has been done on the relation between this process and solubility parameters. In fact it is not clear if the solubility parameter concept is the best approach, although some correlations have been made.[127-129] Hansen[9,11] has used his three-component solubility parameter to characterize pigment surfaces in terms of suspension times. The center for the inorganic (e.g., titanium dioxide) suspension regions in a three-dimensional plot correspond to high solubility parameter values (high surface energies), and some show no suspension in any solvent, but many organic pigments suspend or dissolve in solvents with relatively low solubility parameters. Sedimentation volumes of settled dispersions have also been related to three-component solubility parameters.[130] Skaarup[25] has used a similar approach to mutual interactions between solvent, pigment, and binder.

Hansen,[11] Sorensen,[131,132] and Vinther[133] have reviewed the effect of pigment charges on the dispersion of pigments in solvents, with particular reference to the solubility parameter concept.

E. Liquid Flow Properties

The spreading behavior and film appearance of a coating material on a surface is determined by a large number of factors, many of which are still poorly understood. Approaches to this problem are either empirical and statistical with a large number of test panels, or more basic using solubility parameters, viscosities, volatilities, etc.[118] For example, the surface wetting and dewetting performance of various solvents and surfaces has been correlated with three-component solubility parameters.[125,134]

F. Liquid–Liquid Interfaces: Emulsions

The background to emulsions has been presented by Becher,[135] and Hansen and Beerbower[22] have reported on the use of three-component solubility parameters. The application of solubility parameters to polymeric emulsions in the water-based coatings industry has been reviewed by Seymour and Owen.[136] This subject is also in the qualitative or semiquantitative stage of development.

X. Applications of Solubility Parameters

A. Summary of Recent Applications

Various uses of solubility parameters are summarized in Table VIII. In addition, details of some of those applications not discussed previously are included in the following sections.

B. Solvent Extraction and Infinite Dilution Activity Coefficients

The efficient separation of liquid mixtures by extraction requires a solvent with a high selectivity, i.e., a high value of the ratio of the infinite dilution activity coefficients of the binary components. Weimer and Prausnitz[64] have applied the two-component (polar/nonpolar) solubility parameter method to predict activity coefficients for hydrocarbons at infinite dilution in polar solvents and so predict selectivity of the solvents for one hydrocarbon relative to the other. The cohesive energy density term ($c_{AA} + c_{BB} - 2c_{AB}$) in the Hildebrand–Scatchard expression (37) for the interaction between a polar and a nonpolar substance contains, in addition to polar (τ) and nonpolar (λ) solubility parameters, a term Ψ_{AB} in the induction energy between the polar and nonpolar species. It was found that Ψ_{AB} is related to the polar solubility parameter of the solvent, τ_A, and to the *class* of hydrocarbon but not directly dependent on the solubility parameter of the hydrocarbon solute. For infinitely dilute solutions of saturated hydrocarbons in polar solvents from 0 to 100°C, with τ_A in cal$^{1/2}$ cm$^{-3/2}$

$$\Psi_{AB} = 0.396\tau_A^2 \qquad (74)$$

and the corresponding benzene–polar solvent result is

$$\Psi_{AB} = 0.450\tau_A^2 \qquad (75)$$

The activity coefficient expression, which includes the Flory–Huggins entropy of mixing correction for liquids with greatly different molar volumes (section III.E), is

$$RT \ln \gamma_B = V_B[(\lambda_A - \lambda_B)^2 + \tau_A^2 - 2\Psi_{AB}] + RT[\ln (V_B/V_A) + 1 - V_B/V_A] \qquad (76)$$

TABLE VIII. Some Recent Applications of Solubility Parameters

Application	Reference
Activity coefficients	Section X.B
Aerosol formulation	*a*
Chromatography	Sections VIII.G, IX.C
Coal solvent extraction	*b*
Compressed gases	Section VIII.F
Cosmetics	*c*
Cryogenic solvents	Section V.A.3
Dispersion	Section IX.D
Dyes	Ref 11, *d*
Emulsions	Section IX.F
Gas–liquid solubility	Section X.C
Grease removal	*e*
Membrane permeability	*f*
Paint film appearance	Ref 118
Pharmaceutical	Ref 81, 82, *g*
Pigments	Section IX.D
Plasticizers, polymers, resins	Ref 10, 113, 128
Plasticization	Ref 137
Polymer and plasticizer compatibility	Section X.D
Printing ink	Ref 128
Reaction rate of radical polymerization	*h*
Resistance of plastics to solvents	Ref 109
Rubber blends	*i*
Solid surface characterization	Section IX.B
Solvent extraction	Section X.C
Solvent formulation	Section VIII.E
Surface tension	Section IX.B
Urea–water solutions	Ref 14
Vaporization of plasticizers	*j*
Viscosity of polymer systems	*k*
Water-based polymer systems	Ref 136

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Helpinstill and Van Winkle[85] extended this treatment to include polar–polar binary systems by redefining the quantity Ψ_{AB} as ψ_{AB} to include polar–polar as well as polar–nonpolar interactions, and it was found for polar solvents that to a reasonable approximation

$$\psi_{AB} \propto (\tau_A - \tau_B)^2 \qquad (77)$$

There have been several other extensions of solubility parameter theory to systems of considerable chemical complexity. Freiser and coworkers and Suzuki et al. have applied this concept to organic solvent-water distribution of compounds exhibiting specific interactions[138] and to ion association extraction.[73] Recently Noel and Meloan[139] reported on correlations between the distribution constant, solubility parameters, and physical properties such as refractive index and density for a number of solvent extraction systems. Martire and coworkers[140] have determined infinite dilution activity coefficients for hydrocarbon–hydrocarbon solutions in gas–liquid partition chromatography, and discussed the results in terms of several theorires including the regular solution theory. Kertes[141] has evaluated solubility parameters and activities of long-chain alkylamines and their hydrochlorides.

C. Gas–Liquid Solubility

Hildebrand's solubility parameter method for predicting the solubility of simple gases in regular liquids[2,4] was extended by Prausnitz[47] who considered the gases "condensed" to a hypothetical liquid-like state, with appropriate solubility parameters and molar volumes, which were then mixed with solvent according to liquid miscibility rules. Hansen and Beerbower[22] reproduced a table of "liquid" volumes and solubility parameters for some gaseous solvents. Since most materials which are gaseous under ambient conditions are composed of relatively simple molecules, the solubility parameter concept is reasonably satisfactory as a first approximation for gas–liquid solubility. Exceptions occur where there are specific chemical interactions, as on occasion with HCl, SO_2, and NH_3, for example. Solubility parameters and cohesive energy density have been used recently as the basis of approximate correlations for the solubility of helium[100] and hydrogen[142] in a variety of simple (cryogenic) solvents.

D. Polymer and Plasticizer Compatibility

The compatibility of a particular polymer–plasticizer system is the amount of plasticizer that can be added to the polymer before phase separation occurs. The plasticizer behaves as a solvent for the polymer, and the solubility parameter concept has been applied to this "solution".[96,137] This is also true of polymer compatibility in both liquid and solid phases.[143]

XI. Conclusion

The three-component solubility parameter is theoretically more correct, but the practical results are no better than those given by two-component parameters. In all discussion so far, solvents have been specified as points and solutes as volumes or areas in multicomponent parameter space. It would probably be preferable to treat the solvents also as volumes,[144] even in liquid–liquid interactions, accepting that the solubility parameter does depend on the system used to measure it.

Any approach to the theory of solutions should have one of two clear aims: (i) the development of a fundamental method of studying the thermodynamics and other properties of solutions, with great detail and accuracy, and with the acceptance of complex and cumbersome mathematical descriptions; or (ii) the construction of a practical tool which a solvent formulator can use in his laboratory to simplify his task.

The solubility parameter concept should be associated primarily with aim ii, and should not sacrifice simplicity for accuracy. There is a good thermodynamic reason for this: the Gibbs energy of mixing is made up of two quantities only one of which is described by the solubility parameter. Solubility parameters tell only half the story, even if it is usually the most important half.

If a two-component parameter is adequate for a job, it is preferable to a three-component system in that application. It is nevertheless important for industrial chemists to examine closely the assumptions in the theoretical development of the concept, and for theoreticians to keep in mind possible refinements of practical techniques.

There is a particular problem in the application of solubility parameters to two-phase systems, where neither theoretical nor practical aspects have been adequately developed.

These points have been made strongly by Tawn[145] and by many others, some of whom have communicated with me during the preparation of this review, and whose work has been referred to above. I would like to thank all these people for their assistance.

XII. Glossary of Symbols

Numbers refer to equations in which the symbols first appear.

A	molar Helmholtz energy
A	proportionality constant (8)
$\mathcal{A}$	hydrogen bond accepting capability (45)
A	(subscript) attractive (8)
A, B, C	Antoine equation parameters (59)
$\mathcal{D}$	Hydrogen bond donating capability (45)
$-E$	molar cohesive energy (4)
E	(superscript) excess (29)
F	molar attraction constant (46)
G	molar Gibbs energy
H	(subscript) relating to enthalpy
H	molar enthalpy
H°	standard enthalpy
J	(unit) joule
K	(unit) kelvin
N	(unit) newton
Pa	(unit) pascal, N m^{-2}
R	gas constant
S	molar entropy
S	(subscript) relating to entropy
T	temperature (K)
T	(subscript) constant temperature, isothermal
U	molar internal energy
V	molar volume
V	(subscript) constant volume, isochoric
X	any extensive molar property (14)
X_B	partial molar property of substance B (14)
$X_\mathrm{B}{}^*$	molar property of pure substance B
b	(subscript) relating to atmospheric pressure boiling point
c	cohesive energy density (6)
c	(subscript) critical
d	(subscript) relating to dispersion interactions
f	fractional solubility parameter (54)
f	activity coefficient
f	(subscript) relating to formation
g	(superscript) gas
h	(subscript) relating to hydrogen bonding
k	empirical correction coefficient in geometric mean expression (34)
l	(superscript or subscript) liquid
m	(unit) meter
m	(subscript) relating to mixing
n	amount of substance
n	refractive index
p	pressure
p	fractional polarity (41)
p	(subscript) constant pressure, isobaric
p	(subscript) relating to polar interactions
r	(subscript) reduced
t	temperature (°C)
x	mole fraction
y	activity coefficient on concentration ("molar") scale
$\Delta_\mathrm{l}{}^\mathrm{g}$	change on vaporization
Δ_m	change on mixing
Σ_B	sum over all B
Ψ	induction energy term in solubility parameter (74)
α	isobaric expansivity
β	isochoric thermal pressure coefficient (3)
γ	activity coefficient on molal scale
γ	hydrogen bonding parameter (44)
δ	(one-component) solubility parameter (1)
$\bar{\delta}$	average multi-component solubility parameter (68)
δ_M	solubility parameter in moderately hydrogen-bonded solvent
δ_P	solubility parameter in poorly hydrogen-bonded solvent
δ_S	solubility parameter in strongly hydrogen-bonded solvent
δ_V	volume-dependent solubility parameter (12)
δ_a	association component of solubility parameter (51)
δ_d	dispersion component of solubility parameter (43)
δ_h	hydrogen bonding component of solubility parameter (50)
δ_in	induction component of solubility parameter (43)
δ_o	total solubility parameter (40)
δ_or	orientation component of solubility parameter (43)
δ_p	polar component of solubility parameter (50)
δ_r	residual solubility parameter (13)
ϵ	relative permittivity (65)
ϵ^0	solvent strength parameter (73)
κ	isothermal compressibility
λ	nonpolar solubility parameter (42)
μ	dipole moment
π	internal pressure (3)
ρ	density
ϕ	volume fraction
χ	polymer-solvent interaction parameter (39)
ψ	induction energy term in solubility parameter (77)
ω	Pitzer acentric factor (62)

XIII. Addendum

In the period between the acceptance of this paper and its publication, I have noted the following reports utilizing the concepts of solubility parameter and regular solution.

Section IV.C. "Technique for Reformulating Solvent Mixtures in Epoxy Resin Coatings", G. R. Somerville and J. A. Lopez in "Solvents Theory and Practice", *Advan. Chem. Ser.*, **No. 124,** 175 (1973) (use of fractional polarity).

Section IV.D. "The Application of the Regular Solution Theory to the Ion-Pair Systems", T. Takamatsu, *Bull. Chem. Soc. Jpn.*, **47,** 1287 (1974) (application to solubilities of KCl, KBr, KI, in alcohols).

Section VIII.A. "Solvent Selection via Miscibility Number", N. B. Godfrey, *Chem. Tech.*, 359 (1972).

Section X.A. "Technique for Reformulating Solvent Mixtures in Epoxy Resin Coatings", cited above for section IV.C. "Classification of the Solvent Properties of Common Liquids", L. R. Snyder, *J. Chromatog.*, **92,** 223 (1974) (application to liquid-liquid chromatography). "The Influence of Solvent on Chemical Reactivity", M. R. J. Dack, *J. Chem. Educ.*, **51,** 231 (1974).

Section X.B. "The Screening and Selection of Solvents for the Extraction of Phenol from Water", P. R. Kiezyk and D. Mackay, *Can. J. Chem. Eng.*, **51,** 741 (1973). "Solvent Selectivity for Hydrocarbons with Close Molar Volumes", W. A. Spelyng and D. P. Tassios, *Ind. Eng. Chem., Proc. Des. Dev.*, **13,** 328 (1974).

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