

CRC

HANDBOOK
of
SOLUBILITY
PARAMETERS
and
OTHER COHESION
PARAMETERS

Second Edition

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CRC

PRESS

Library of Congress Cataloging-in-Publication Data

Barton, Allan F. M.

CRC handbook of solubility parameters and other cohesion
parameters / Allan F. M. Barton. -- 2nd ed.

p. cm.

Includes bibliographical references and index.

ISBN 0-8493-0176-9

1. Solubility. 2. Cohesion. I. Title

QD543.B22 1991

541.3'42--dc20

91-18630
CIP

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International Standard Book Number 0-8493-0176-9

Library of Congress Card Number 91-18630

Printed in the United States of America 1 2 3 4 5 6 7 8 9 0

THERMODYNAMICS

Molecular materials exist as liquids and solids over certain ranges of temperature and pressure because in some circumstances the liquid and solid states are more stable than the gaseous state; that is, there are energetic advantages in having the molecules arranged in either random or ordered close-packed configurations. In these condensed phases, the strong attractive or cohesive forces existing between the molecules give rise to considerable negative potential energies relative to vapor phase molecules which have negligible potential energy arising in this way. (Ionic liquids and crystals have even stronger attractive forces arising from coulombic interactions.)

2.1 COHESIVE ENERGY

If U is defined as the molar internal energy (the molar potential energy of a material relative to the ideal vapor at the same temperature), then U has a numerically negative value for a condensed material. It follows, therefore, that the molar *cohesive energy* (the energy associated with the net attractive interactions of the material and defined as $-U$) has a positive value.

For a liquid, if it is assumed that the intramolecular properties (those associated with individual molecules) are identical in gaseous and liquid states (which is true except in the case of complex molecules: see Section 14.9) it can be seen that the molar cohesive energy can be divided into two parts:

1. The molar vaporization energy, ${}_1\Delta_g U$, required to vaporize one mole of the liquid to its saturated vapor
2. The energy, ${}_g\Delta_\infty U$, required to expand the saturated vapor to infinite volume at constant temperature; that is, the energy necessary to completely separate the molecules

As presented by Polak,¹ this can be expressed

$$-U = {}_1\Delta_g U + {}_g\Delta_\infty U = {}_1\Delta_g U + \int_{V_g}^{V=\infty} (\partial U/\partial V)_T dV \quad (1)$$

where V is the molar volume. The molar cohesive energy $-U$ can be subdivided also according to the relationship

$$-U = {}_1\Delta_g H + {}_g\Delta_\infty H - RT + p_s {}^lV \quad (2)$$

where ${}_1\Delta_g H$ is the molar vaporization enthalpy; ${}_g\Delta_\infty H$ is the enthalpy change (increase) on isothermally expanding 1 mol of saturated vapor to zero pressure; p_s is the saturation vapor pressure at temperature T ; lV is the molar volume of the liquid (the superscript l is frequently omitted if there is no chance of ambiguity); and R gas constant ($8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$). At pressures below atmospheric pressure (that is, at temperatures below the normal boiling point) ${}_g\Delta_\infty H$ and $p_s {}^lV$ are usually negligible compared with ${}_1\Delta_g H$ and RT :

$$-U = {}_1\Delta_g U = {}_1\Delta_g H - RT \quad (3)$$

However, at higher pressures the other terms cannot be neglected, and in fact at the critical point ${}_1\Delta_g H$ is zero, so Equation 3 erroneously leads to a negative value for the cohesive

energy while the full Equation 2 correctly predicts a small positive cohesive energy at the critical point. Values of ${}_1\Delta_g H$, ${}_1\Delta_g U$, and $-U$ for various liquids at their normal boiling points in Table 1 illustrates typical variations in these quantities.

Svoboda and co-workers²⁻⁷ have recently considered the cohesive energies of liquids in some detail, and Table 2 summarizes their recommended 25°C values.

2.2 COHESIVE PRESSURE AND THE HILDEBRAND PARAMETER

The stabilizing or cohesive effect in condensed phases can be expressed in terms of the *cohesive pressure* which is dimensionally identical with the *cohesive energy density* (cohesive energy per unit volume),

$$c = -U/V \quad (4)$$

Cohesive energy density was the basis of the original definition by Hildebrand and Scott⁸⁻¹⁰ of what is now generally called the Hildebrand solubility parameter or *Hildebrand parameter*,

$$\delta = c^{1/2} = (-U/V)^{1/2} \approx ({}_1\Delta_g U/V)^{1/2} \quad (5)$$

This parameter was intended for nonpolar, nonassociating systems, but the concept has been extended to all types of systems.

The term "solubility" parameter, which has been used widely, is really too restrictive for a quantity that may be used to correlate such a wide range of physical and chemical properties.¹¹ The name "cohesion parameter" is preferred by the author for the group of parameters with dimensions of (pressure)^{1/2} that includes the Hildebrand parameter as defined in Equation 5. Use of the proposed alternative title "interaction parameter"¹² would result in confusion with the polymer-liquid interaction parameter χ (Chapter 13) and several other binary interaction parameters characterizing *pairs* of substances.

The title "solubility parameter" and the form of Equation 5 suggest a close link between the phenomena of "solubility" or "miscibility" and those of "cohesion" and "vaporization." This similarity can be appreciated by considering what happens in a mixing process: the "like" molecules of each component in a mixture become separated from one another by what approximates to an infinite distance, comparable in some respects to what happens in the vaporization process. The Hildebrand parameter is sometimes called the "total" cohesion parameter, δ_t , because there are various "component" cohesion parameters, but the subscript "t" is usually omitted if this can be done without ambiguity.

From Equations 3 and 5 it is clear that the Hildebrand parameter of a liquid may be readily evaluated if the molar volume and molar vaporization enthalpy have been determined at the required temperature, and if that temperature is well below the normal boiling point of the liquid:

$$\delta = ({}_1\Delta_g H - RT)^{1/2}/V^{1/2} \quad (6)$$

This density and enthalpy information is readily available for some liquids, but for many other liquids and for all polymers, solids, and surfaces it is necessary to use indirect evaluation methods, described in subsequent chapters, for the estimation of cohesion parameters.

Table 3 lists selected values of Hildebrand parameters, molar volumes and molar vaporization enthalpies at 25°C, reported by Hildebrand, Prausnitz, and Scott¹⁰ and presented here in SI units (see Section 2.5). The vaporization enthalpies are corrected for expansion

TABLE 1
Calculated Values of Molar Vaporization Enthalpies, Molar Vaporization
Energies and Molar Cohesive Energies for Liquids at their Normal Boiling
Points

| ND | Liquid | $t_b/^\circ\text{C}$ | $\Delta_v H/\text{kJ mol}^{-1}$ | $\Delta_v U/\text{kJ mol}^{-1}$ | $-U/\text{kJ mol}^{-1}$ |
|-----|---|----------------------|---------------------------------|---------------------------------|-------------------------|
| | Acetone, 2-propanone | 56.1 | 29.7 | 27.0 | 27.2 |
| | Ammonia | -33.3 | 23.5 | 21.5 | 21.7 |
| | Aniline | 184.2 | 43.9 | 40.2 | 40.5 |
| | Benzene | 80.1 | 30.8 | 27.9 | 28.2 |
| | Bromine | 58.7 | 29.3 | 26.6 | 26.8 |
| | Bromobenzene | 155.9 | 37.6 | 34.2 | 34.5 |
| | Bromoethane, ethyl bromide | 38.4 | 26.8 | 24.3 | 24.5 |
| (4) | Butane | -0.5 | 22.4 | 20.3 | 20.5 |
| | 1-Butanol | 117.5 | 43.6 | 40.5 | 40.8 |
| | 2-Butanol | 108.0 | 42.9 | 39.9 | 40.2 |
| | tert-Butanol | 82.9 | 39.9 | 37.1 | 37.4 |
| | 1-Butene | -6.3 | 22.1 | 20.0 | 20.2 |
| | cis-2-Butene | 3.7 | 23.3 | 21.1 | 21.3 |
| | trans-2-Butene | 0.9 | 22.8 | 20.6 | 20.8 |
| (5) | Carbon disulfide | 46.2 | 26.7 | 24.1 | 24.3 |
| | Chlorobenzene | 131.7 | 35.4 | 32.2 | 32.5 |
| | Chloroethane, ethyl chloride | 12.2 | 24.6 | 22.3 | 22.5 |
| | 1-Chloropropane, propyl chloride | 46.6 | 27.5 | 25.0 | 25.2 |
| | o-Cresol, 2-methylphenol | 190.8 | 45.5 | 41.8 | 42.2 |
| | m-Cresol, 3-methylphenol | 202.2 | 48.1 | 44.2 | 44.6 |
| | p-Cresol, 4-methylphenol | 201.8 | 48.0 | 44.2 | 44.5 |
| | Cyclohexane | 80.7 | 30.0 | 27.2 | 27.4 |
| | Cyclopentane | 49.3 | 27.3 | 24.7 | 25.0 |
| | 1,2-Dibromoethane, ethylene dibromide | 131.5 | 36.1 | 32.8 | 33.1 |
| | Dichlorodifluoromethane | -29.8 | 20.1 | 18.1 | 18.3 |
| | 1,1-Dichloroethane | 57.3 | 29.0 | 26.3 | 26.6 |
| | 1,2-Dichloroethane, ethylene dichloride | 83.7 | 32.2 | 29.3 | 29.5 |
| | Dichloromethane | 39.8 | 28.1 | 25.6 | 25.8 |
| | Diethyl ether | 34.6 | 26.5 | 24.1 | 24.3 |
| | Dimethylamine | 6.9 | 24.7 | 22.5 | 22.7 |
| | 2,2-Dimethylbutane | 49.7 | 26.3 | 23.7 | 24.0 |
| | 2,3-Dimethylbutane | 58.0 | 27.3 | 24.7 | 25.0 |
| | Dimethyl ether | -24.8 | 21.5 | 19.5 | 19.7 |
| | 2,2-Dimethylpropane, neopentane | 9.5 | 22.7 | 20.5 | 20.8 |
| | Ethanol | 78.3 | 39.4 | 36.6 | 36.9 |
| | Ethyl acetate | 77.1 | 32.1 | 29.4 | 29.7 |
| | Ethylbenzene | 136.2 | 35.8 | 32.5 | 32.9 |
| | Ethyl formate | 54.0 | 29.9 | 27.3 | 27.5 |
| | Ethyl propionate | 98.9 | 33.9 | 31.0 | 31.3 |
| | Heptane | 98.4 | 31.9 | 28.9 | 29.3 |
| | Hexane | 68.7 | 28.9 | 26.2 | 26.6 |
| | 1-Hexene | 63.3 | 28.3 | 25.7 | 26.0 |
| | cis-2-Hexene | 68.8 | 29.0 | 26.3 | 26.6 |
| | trans-2-Hexene | 68.0 | 28.9 | 26.2 | 26.5 |
| | cis-3-Hexene | 66.8 | 28.8 | 26.1 | 26.4 |
| | trans-3-Hexene | 67.3 | 29.0 | 26.3 | 26.6 |
| (6) | Hydrazine | 113.1 | 41.5 | 38.4 | 38.5 |
| | 2-Propanol | 82.2 | 40.6 | 37.8 | 38.1 |
| | Methanol | 64.5 | 36.4 | 33.7 | 33.9 |
| | Methyl acetate | 56.9 | 30.4 | 27.7 | 28.0 |
| | Methylamine | -6.4 | 26.2 | 24.0 | 24.2 |
| | 2-Methylbutane, isopentane | 27.9 | 24.7 | 22.3 | 22.6 |
| | Methyl formate | 31.8 | 28.5 | 26.0 | 26.2 |

TABLE 1 (continued)
 Calculated Values of Molar Vaporization Enthalpies, Molar Vaporization Energies and Molar Cohesive Energies for Liquids at their Normal Boiling Points

| Liquid | $t_b/^\circ\text{C}$ | $\Delta_v H/\text{kJ mol}^{-1}$ | $\Delta_v U/\text{kJ mol}^{-1}$ | $-U/\text{kJ mol}^{-1}$ |
|---------------------------------------|----------------------|---------------------------------|---------------------------------|-------------------------|
| 2-Methylpentane | 60.3 | 27.9 | 25.2 | 25.5 |
| 2-Methylpropane, isobutane | -11.4 | 21.2 | 19.1 | 19.3 |
| 2-Methylpropene, isobutylene | -6.9 | 22.1 | 20.0 | 20.2 |
| Methyl propionate | 79.4 | 32.1 | 29.3 | 29.6 |
| Octane | 125.7 | 34.6 | 31.4 | 31.9 |
| Pentane | 36.1 | 25.8 | 23.4 | 23.7 |
| 1-Pentene | 29.5 | 25.3 | 22.9 | 23.1 |
| cis-2-Pentene | 36.5 | 26.4 | 23.9 | 24.1 |
| trans-2-Pentene | 36.3 | 26.1 | 23.7 | 24.0 |
| Phenol | 181.8 | 46.6 | 43.0 | 43.4 |
| Propane | -42.1 | 18.8 | 17.0 | 17.1 |
| 1-Propanol | 97.2 | 41.1 | 38.4 | 38.7 |
| Propionic acid | 141.0 | 42.3 | 39.0 | 39.3 |
| Propyl acetate | 101.5 | 34.1 | 31.2 | 31.5 |
| Propylene, propene | -47.7 | 18.5 | 16.7 | 16.8 |
| Tetrachloromethane | 76.6 | 30.4 | 27.6 | 27.9 |
| 1,2,3,5-Tetramethylbenzene | 198.0 | 42.5 | 38.8 | 39.2 |
| 1,2,4,5-Tetramethylbenzene | 196.8 | 42.4 | 38.7 | 39.1 |
| Toluene, methylbenzene | 110.6 | 33.4 | 30.3 | 30.6 |
| Trichloromethane, chloroform | 61.7 | 29.1 | 26.4 | 26.7 |
| Trimethylamine | 2.9 | 24.1 | 21.9 | 22.1 |
| 1,2,3-Trimethylbenzene | 176.1 | 39.9 | 36.3 | 36.7 |
| 1,2,4-Trimethylbenzene | 169.4 | 39.3 | 35.8 | 36.2 |
| Water | 100.0 | 40.8 | 37.8 | 37.9 |
| <i>o</i> -Xylene, 1,2-dimethylbenzene | 144.4 | 36.7 | 33.4 | 33.7 |
| <i>m</i> -Xylene, 1,3-dimethylbenzene | 139.1 | 36.2 | 32.9 | 33.3 |
| <i>p</i> -Xylene, 1,4-dimethylbenzene | 138.3 | 35.9 | 32.7 | 33.0 |

Adapted from Polak, J., *Collect. Czech. Chem. Commun.*, 31, 1483, 1966

to the ideal gas state where possible. Substances that are solids at 25°C have been treated as subcooled liquids (see Chapter 12). Similar information on cohesive energy densities was provided by Varushchenko, Loseva, and Druzhina⁴¹ for 1,1-, 1,1- and α,ω -dichloro-*n*-alkanes, from which the Hildebrand parameters in Table 3a were evaluated.

The basis of the cohesion parameter approach to interactions may be stated as follows. A material with a high δ value requires more energy for dispersal than is gained by mixing it with a material of low cohesion parameter, so immiscibility results. On the other hand, two materials with similar δ values gain sufficient energy on mutual dispersion to permit mixing. This concept is attractive for practical applications because it aims to predict the properties of a *system* using only the properties of its individual *components*: in principle no information on the properties of the mixed system is required.

It is necessary to emphasize that the Hildebrand parameter is fundamentally a liquid state property. When gases are considered (Chapter 11) they are treated as hypothetical "liquid" solutes at atmospheric pressure, and substances that are solids at normal temperatures are treated as subcooled liquids (Chapter 12). As defined here, Hildebrand parameters cannot be calculated directly from vaporization enthalpies or sublimation enthalpies without taking into account their liquid-state basis. Lawson's list of "solubility parameters" of the elements^{13,14} (Table 4) is a useful set of *cohesion* parameters, (although they are not *Hildebrand* parameters if they are calculated directly from enthalpies of vaporization or sub-

TABLE 2
Rounded Values of Cohesive Energies at 25°C

| | Formula | Compound | $-U/\text{kJ mol}^{-1}$ |
|------|------------------------------|-----------------------------------|-------------------------|
| 25.5 | C_2H_6 | Ethane | 7.7 |
| 19.3 | C_3H_8 | Propane | 13.9 |
| 20.2 | C_4H_{10} | Butane | 19.2 |
| 29.6 | | Isobutane | 17.6 |
| 31.9 | C_5H_{12} | Pentane | 24.3 |
| 23.7 | | Isopentane | 22.8 |
| 23.1 | | Neopentane | 19.9 |
| 24.1 | C_6H_{14} | Hexane | 29.3 |
| 24.0 | | Branched hexanes | 26—28 |
| 43.4 | C_7H_{16} | Heptane | 34.2 |
| 17.1 | | Branched heptanes | 30—33 |
| 38.7 | C_8H_{18} | Octane | 39.1 |
| 39.3 | | Branched octanes | 33—41 |
| 31.5 | C_9H_{20} | Nonane | 44.0 |
| 16.8 | | Branched nonanes | 36—40 |
| 27.9 | $\text{C}_{10}\text{H}_{22}$ | Decane | 48.9 |
| 39.2 | | Branched decanes | 45—47 |
| 39.1 | $\text{C}_{11}\text{H}_{24}$ | Undecane | 54.0 |
| 30.6 | | Branched undecanes | 48—52 |
| 26.7 | $\text{C}_{12}\text{H}_{26}$ | Dodecane | 59.0 |
| 22.1 | | 2,2,4,6,6-Pentamethylheptane | 46.5 |
| 36.7 | $\text{C}_{13}\text{H}_{28}$ | Tridecane | 64.0 |
| 36.2 | $\text{C}_{14}\text{H}_{30}$ | Tetradecane | 68.8 |
| 37.9 | $\text{C}_{15}\text{H}_{32}$ | Pentadecane | 73.6 |
| 33.7 | $\text{C}_{16}\text{H}_{34}$ | Hexadecane | 78.9 |
| 33.3 | $\text{C}_{17}\text{H}_{36}$ | Heptadecane | 83.5 |
| 33.0 | C_3H_6 | Cyclopropane | 15.7 |
| | C_4H_8 | Cyclobutane | 21.5 |
| | C_5H_8 | Spiropentane | 25.2 |
| | C_5H_{10} | Cyclopentane | 26.3 |
| | C_6H_{12} | Cycloalkanes | 29—31 |
| | C_7H_{12} | 1-Methylbicyclo[3.1.0]hexane | 32.4 |
| | C_7H_{14} | Cycloalkanes | 32—34 |
| | C_8H_{16} | Cycloalkanes | 36—39 |
| | C_9H_{16} | 1,4-Dimethylbicyclo[2.2.1]heptane | 36.4 |
| | C_9H_{18} | Cycloalkanes | 42—43 |
| | $\text{C}_{10}\text{H}_{20}$ | Cycloalkanes | 45 |
| | $\text{C}_{11}\text{H}_{22}$ | Pentylcyclohexane | 51.4 |
| | $\text{C}_{12}\text{H}_{22}$ | Cyclohexylcyclohexane | 55.5 |
| | C_3H_6 | Propylene | 13.7 |
| | C_4H_6 | 1,2-Butadiene | 21.2 |
| | | 1,3-Butadiene | 19.0 |
| | | 1-Butyne | 21.3 |
| | C_4H_8 | 1-Butene | 18.4 |
| | | 2-Butenes | 20 |
| | C_5H_{10} | Alkenes | 23—25 |
| | C_6H_{12} | 2,3-Dimethyl-2-butene | 30.2 |
| | C_8H_{14} | Alkynes | 40—42 |
| | C_8H_{16} | 1-Octene | 38.0 |
| | $\text{C}_{10}\text{H}_{20}$ | 1-Decene | 48.0 |
| | $\text{C}_{12}\text{H}_{24}$ | 1-Dodecene | 58.3 |
| | $\text{C}_{16}\text{H}_{32}$ | 1-Hexadecene | 77.8 |
| | C_6H_6 | Benzene | 31.5 |
| | C_6H_{10} | Cyclohexene | 31.1 |
| | C_7H_8 | Toluene | 35.6 |
| | C_8H_{10} | Alkylbenzenes | 40—41 |

TABLE 2 (continued)
Rounded Values of Cohesive Energies at 25°C

| Formula | Compound | $-U/\text{kJ mol}^{-1}$ |
|---------------------------------------|--|-------------------------|
| C_8H_{12} | 4-Vinyl-4-cyclohexene | 37.1 |
| | <i>cis, cis</i> -1,5-Cyclooctadiene | 40.9 |
| C_9H_{10} | Alkylbenzenes | 43—48 |
| | <i>cis</i> -5-Ethylidenebicyclo[2.2.1]-2-heptene | 41.7 |
| C_9H_{14} | 2,3-Dimethylbicyclo[2.2.1]-2-heptene | 39.7 |
| $\text{C}_{10}\text{H}_{14}$ | Alkylbenzenes | 45—49 |
| $\text{C}_{12}\text{H}_{16}$ | Cyclohexylbenzene | 57.5 |
| C_6F_6 | Hexafluorobenzene | 33.3 |
| C_6HF_5 | Pentafluorobenzene | 33.9 |
| $\text{C}_6\text{H}_4\text{F}_2$ | Difluorobenzenes | 32—34 |
| $\text{C}_6\text{H}_5\text{F}$ | Fluorobenzene | 32.2 |
| $\text{C}_7\text{H}_3\text{F}_5$ | 2,3,4,5,6-Pentafluorotoluene | 38.7 |
| $\text{C}_7\text{H}_3\text{F}_3$ | (Trifluoromethyl)benzene | 35.2 |
| $\text{C}_7\text{H}_7\text{F}$ | 4-Fluorotoluene | 37.0 |
| C_8F_{18} | Octadecafluorooctane | 38.7 |
| $\text{C}_8\text{H}_{17}\text{F}$ | 1-Fluorooctane | 47.2 |
| C_9F_{18} | Octadecafluoropropylcyclohexane | 40.6 |
| $\text{C}_{10}\text{F}_{18}$ | Octadecafluorodecahydronaphthalenes | 43 |
| $\text{C}_{10}\text{F}_{20}$ | Perfluoro-2-methylpropylcyclohexane | 44.3 |
| CCl_4 | Tetrachloromethane | 30.1 |
| CHCl_3 | Trichloromethane | 28.9 |
| CH_2Cl_2 | Dichloromethane | 26.5 |
| C_2Cl_4 | Tetrachloroethylene | 37.2 |
| C_2HCl_3 | Trichloroethylene | 32.1 |
| $\text{C}_2\text{H}_2\text{Cl}_2$ | 1,1-Dichloroethylene | 24.3 |
| $\text{C}_2\text{H}_2\text{Cl}_4$ | 1,1,2,2-Tetrachloroethane | 43.3 |
| $\text{C}_2\text{H}_3\text{Cl}_3$ | 1,1,1-Trichloroethane | 30.1 |
| | 1,1,2-Trichloroethane | 37.8 |
| $\text{C}_2\text{H}_4\text{Cl}_2$ | 1,1-Dichloroethane | 28.3 |
| | 1,2-Dichloroethane | 32.7 |
| $\text{C}_3\text{H}_6\text{Cl}_2$ | 1,3-Dichloropropane | 38.3 |
| $\text{C}_3\text{H}_7\text{Cl}$ | 1-Chloropropane | 26.1 |
| $\text{C}_4\text{H}_8\text{Cl}_2$ | 1,2-Dichlorobutane | 37.1 |
| | 1,4-Dichlorobutane | 43.9 |
| $\text{C}_4\text{H}_9\text{Cl}$ | 1-Chlorobutane | 31.2 |
| | Isobutyl chloride | 29.3 |
| | <i>sec</i> -Butyl chloride, 2-chlorobutane | 29.2 |
| | <i>tert</i> -Butyl chloride | 26.7 |
| $\text{C}_5\text{H}_{10}\text{Cl}_2$ | 1,2-Dichloropentane | 41.4 |
| | 1,5-Dichloropentane | 48.2 |
| $\text{C}_5\text{H}_{11}\text{Cl}$ | Chloropentanes | 34—36 |
| $\text{C}_6\text{H}_5\text{Cl}$ | Chlorobenzene | 38.5 |
| $\text{C}_6\text{H}_{12}\text{Cl}_2$ | 1,2-Dichlorohexane | 45.7 |
| $\text{C}_6\text{H}_{13}\text{Cl}$ | 1-Chlorohexane | 40.4 |
| $\text{C}_7\text{H}_{13}\text{Cl}$ | 1-Chloroheptane | 45.2 |
| $\text{C}_8\text{H}_{17}\text{Cl}$ | 1-Chlorooctane | 49.9 |
| $\text{C}_{12}\text{H}_{25}\text{Cl}$ | 1-Chlorododecane | 68.7 |
| $\text{C}_{16}\text{H}_{33}\text{Cl}$ | 1-Chlorohexadecane | 89.3 |
| CHBr_3 | Tribromomethane | 43.6 |
| CH_2Br_2 | Dibromomethane | 34.6 |
| CH_3Br | Bromomethane | 20.8 |
| $\text{C}_2\text{H}_4\text{Br}_2$ | 1,2-Dibromoethane | 39.3 |
| $\text{C}_2\text{H}_5\text{Br}$ | Bromoethane | 25.8 |
| $\text{C}_3\text{H}_5\text{Br}$ | Allyl bromide | 30.4 |
| $\text{C}_3\text{H}_6\text{Br}_2$ | 1,2-Dibromopropane | 39.2 |
| | 1,3-Dibromopropane | 45.0 |

TABLE 2 (continued)
Rounded Values of Cohesive Energies at 25°C

| Formula | Compound | -U/kJ mol ⁻¹ |
|--|--|-------------------------|
| C ₃ H ₇ Br | Bromopropanes | 28—30 |
| C ₄ H ₉ Br ₂ | 1,4-Dibromobutane | 50.6 |
| | 1,2-Dibromo-2-methylpropane | 40.9 |
| C ₄ H ₉ Br | Alkyl bromides | 30—34 |
| C ₅ H ₁₁ Br | 1-Bromopentane | 38.8 |
| C ₆ H ₅ Br | Bromobenzene | 42.1 |
| C ₆ H ₁₃ Br | 1-Bromoheptane | 43.4 |
| C ₇ H ₁₅ Br | 1-Bromoheptane | 48.1 |
| C ₈ H ₁₇ Br | 1-Bromooctane | 53.3 |
| C ₁₂ H ₂₅ Br | 1-Bromododecane | 72.3 |
| C ₁₆ H ₃₃ Br | 1-Bromohexadecane | 91.9 |
| C ₂ H ₅ I | Iodoethane | 29.6 |
| C ₃ H ₇ I | Iodopropanes | 32—34 |
| C ₄ H ₉ I | Iodobutanes | 33—38 |
| C ₅ H ₁₁ I | 1-Iodopentane | 42.8 |
| C ₆ H ₁₃ I | 1-Iodoheptane | 47.3 |
| C ₂ Br ₂ ClF ₃ | 1,2-Dibromochlorotrifluoroethane | 32.6 |
| C ₂ Br ₂ F ₄ | 1,2-Dibromotetrafluoroethane | 26.1 |
| C ₂ Cl ₂ F ₃ | Trichlorotrifluoroethanes | 26 |
| C ₂ HBrClF ₃ | Bromochlorotrifluoroethanes | 27—28 |
| C ₂ H ₄ BrCl | 1-Bromo-2-chloroethane | 35.7 |
| C ₃ Cl ₂ F ₆ | 1,2-Dichlorohexafluoropropane | 24.8 |
| C ₃ H ₂ Cl ₃ F ₃ | 1,1,1-Trichloro-3,3,3-trifluoropropane | 34.3 |
| C ₃ H ₃ Cl ₂ F ₃ | 1,1-Dichloro-3,3,3-trifluoropropane | 31.7 |
| C ₃ H ₆ BrCl | 1-Bromo-3-chloropropane | 41.6 |
| C ₆ ClF ₅ | Chloropentafluorobenzene | 38.6 |
| CH ₃ N | Methylamine | 21.4 |
| C ₂ H ₇ N | Dimethylamine | 23.0 |
| C ₂ H ₈ N ₂ | 1,2-Ethanediamine, ethylene diamine | 42.5 |
| C ₃ H ₉ N | Propylamine | 29.0 |
| | Isopropylamine | 26.2 |
| | Trimethylamine | 19.7 |
| C ₃ H ₁₀ N ₂ | 1,3-Propanediamine | 47.7 |
| | <i>N</i> -Methyl-1,2-ethanediamine | 42.7 |
| C ₄ H ₁₁ N | Butylamines | 29—33 |
| C ₅ H ₁₃ N | Propylamines | 31—38 |
| C ₆ H ₇ N | Aniline | 53.4 |
| C ₆ H ₁₃ N | Cyclohexylamine | 41.2 |
| C ₆ H ₁₅ N | Hexylamines | 32—43 |
| C ₇ H ₉ N | Benzylamine | 57.7 |
| C ₇ H ₁₇ N | Heptylamines | 40—48 |
| C ₈ H ₁₁ N | <i>N,N</i> -Dimethylaniline | 50.4 |
| C ₈ H ₁₉ N | Octylamines | 47—50 |
| C ₉ H ₂₁ N | Tripropylamine | 43.7 |
| C ₂ N ₂ | Ethanedinitrile | 18.4 |
| C ₂ H ₃ N | Ethanenitrile, acetonitrile | 30.9 |
| C ₃ H ₅ N | Propanenitrile, propionitrile | 33.7 |
| C ₄ H ₅ N | Butanenitriles, allyl cyanide | 37—38 |
| | Cyclopropanecarbonitrile | 39.5 |
| C ₄ H ₇ N | Butanenitriles | 35—37 |
| C ₅ H ₇ N | Pentanenitriles | 41—43 |
| | Cyclobutanecarbonitrile | 41.9 |
| C ₅ H ₉ N | Pentanenitriles | 35—41 |
| C ₆ H ₇ N | 1-Cyclopentene carbonitrile | 42.5 |
| C ₆ H ₉ N | Cyclopentane carbonitrile | 41.0 |
| C ₆ H ₁₁ N | Hexanenitrile, capronitrile | 45.4 |

TABLE 2 (continued)
Rounded Values of Cohesive Energies at 25°C

| Formula | Compound | -U/kJ mol ⁻¹ |
|--|---|-------------------------|
| C ₇ H ₉ N | 1-Cyclohexenecarbonitrile | 51.1 |
| C ₇ H ₁₁ N | Cyclohexanecarbonitrile | 49.4 |
| C ₈ H ₁₃ N | Octanenitrile | 54.3 |
| C ₁₀ H ₁₉ N | Decanenitrile | 64.4 |
| C ₁₁ H ₂₁ N | Undecanenitrile | 68.7 |
| C ₁₂ H ₂₃ N | Dodecanenitrile | 73.6 |
| C ₁₄ H ₂₇ N | Tetradecanenitrile | 82.8 |
| C ₄ H ₄ N ₂ | Pyridazine | 51.0 |
| | Pyrimidine | 47.3 |
| | Pyrrole | 42.9 |
| C ₄ H ₉ N | Pyrrolidine | 35.0 |
| C ₅ H ₇ N | Pyridine | 37.7 |
| C ₆ H ₇ N | Methylpyridines, picoline | 40—42 |
| C ₇ H ₉ N | Dimethylpyridines | 43—48 |
| C ₈ H ₁₁ N | Trimethylpyridines | 48 |
| C ₈ H ₁₆ N ₂ | 3,3,6,6-Tetramethyl-3,4,5,6-tetrahydropyridazine | 47.6 |
| CH ₆ N ₂ | Methylhydrazine | 38.0 |
| C ₇ H ₈ N ₂ | Dimethylhydrazines | 33—37 |
| C ₃ H ₁₂ N ₂ | 1-(Methylazo)butane | 33.9 |
| C ₆ H ₁₄ N ₂ | Azopropane | 37.4 |
| | 2-(Isopropylazo)propane | 33.4 |
| C ₈ H ₁₈ N ₂ | Azobutane | 46.8 |
| | 2-(<i>tert</i> -Butylazo)-2-methylpropane | 36.6 |
| C ₁₂ H ₂₆ N ₂ | 2-(<i>tert</i> -Butylazo)-2,4,4-trimethylpentane | 51.1 |
| C ₁₆ H ₃₄ N ₂ | 2,2'-Azo-(2,4,4-trimethylpentane) | 64.1 |
| C ₂ H ₆ O | Dimethyl ether | 16.8 |
| C ₄ H ₁₀ O | Ethers | 25 |
| C ₄ H ₁₀ O ₂ | 1,2-Dimethoxyethane | 34.0 |
| C ₃ H ₁₂ O | Butyl methyl ethers | 28—30 |
| | Ethyl propyl ethers | 28—29 |
| C ₅ H ₁₂ O ₂ | 1-Ethoxy-2-methoxyethane | 37.4 |
| | Diethoxymethane | 33.3 |
| C ₆ H ₁₂ O | Butyl vinyl ethers | 32—34 |
| C ₆ H ₁₄ O | Methyl pentyl ethers | 33—34 |
| | Butyl ethyl ethers | 31—34 |
| | Dipropyl ethers | 30—33 |
| C ₆ H ₁₄ O ₂ | 2-Methoxy-1-propoxyethane | 41.2 |
| | Diethoxyethane | 40.8 |
| C ₆ H ₁₄ O ₃ | Bis(ethoxymethyl)ether | 42.2 |
| C ₇ H ₈ O | Methyl phenyl ether | 44.4 |
| C ₇ H ₁₆ O | Ethers | 32—40 |
| C ₇ H ₁₆ O ₂ | Diethers | 43—45 |
| C ₇ H ₁₆ O ₄ | 3,5,7,9-Tetraoxoundecane | 51.2 |
| C ₈ H ₁₀ O | Ethyl phenyl ether | 48.6 |
| C ₈ H ₁₈ O | Ethers | 35—44 |
| C ₈ H ₁₈ O ₂ | Diethers | 48—49 |
| C ₈ H ₁₈ O ₃ | Diethylene glycol diethyl ether | 55.9 |
| C ₉ H ₂₀ O | Ethers | 42—50 |
| C ₉ H ₂₀ O ₂ | 1-Butoxy-2-propoxyethane | 52.2 |
| C ₁₀ H ₂₂ O | Ethers | 48—55 |
| C ₁₀ H ₂₂ O ₂ | 1,2-Dibutoxyethane | 56.3 |
| C ₁₁ H ₂₄ O | Ethers | 58—60 |
| C ₁₂ H ₂₆ O | Ethers | 62—63 |
| CH ₄ O | Methanol | 35.4 |
| C ₂ H ₆ O | Ethanol | 40.0 |
| C ₃ H ₈ O | 1-Propanol | 45.0 |
| | 2-Propanol | 43.0 |

TABLE 2 (continued)
Rounded Values of Cohesive Energies at 25°C

| Formula | Compound | -U/kJ mol ⁻¹ |
|--|--|-------------------------|
| C ₄ H ₁₀ O | 1-Butanol | 49.9 |
| | Other butanols | 44—48 |
| C ₅ H ₁₀ O | Cyclopentanol | 55.2 |
| C ₅ H ₁₂ O | 1-Pentanol | 54.6 |
| | Other pentanols | 48—53 |
| C ₆ H ₁₂ O | Cyclohexanol | 59.5 |
| C ₆ H ₁₄ O | 1-Hexanol | 59.1 |
| | Other hexanols | 52—58 |
| C ₇ H ₁₆ O | 1-Heptanol | 64.3 |
| C ₈ H ₁₀ O | Dimethylphenols | 62—80 |
| C ₈ H ₁₈ O | 1-Octanol | 68.5 |
| C ₉ H ₂₀ O | 1-Nonanol | 74.4 |
| C ₁₀ H ₂₂ O | 1-Decanol | 79.0 |
| C ₁₁ H ₂₄ O | 1-Dodecanol | 89.5 |
| C ₁₄ H ₃₀ O | 1-Tetradecanol | 99.7 |
| C ₂ H ₄ O | Ethanal, acetaldehyde | 23.7 |
| C ₃ H ₆ O | Propanal | 27.5 |
| | 2-Propanone, acetone | 28.8 |
| C ₄ H ₈ O | 2-Butanone, methyl ethyl ketone | 32.4 |
| C ₅ H ₈ O | Cyclopentanone | 40.3 |
| | Cyclopropyl methyl ketone | 37.0 |
| C ₅ H ₈ O ₂ | 2,4-Pentanedione | 40 |
| C ₅ H ₁₀ O | Pentanones | 34—36 |
| C ₆ H ₁₀ O | Cyclohexanone | 43.4 |
| C ₆ H ₁₂ O | Hexanones | 36—41 |
| C ₇ H ₁₀ O | Dicyclopropyl ketone | 51.2 |
| C ₇ H ₁₄ O | Heptanones | 39—45 |
| C ₈ H ₁₆ O | 2,2,4-Trimethyl-3-pentanone | 40.8 |
| C ₉ H ₁₄ O | 2-Hexahydroindanone | 54—55 |
| C ₉ H ₁₆ O | Dimethyl-3,5-heptanediones | 53.6 |
| C ₉ H ₁₈ O | Nonanones | 43—54 |
| C ₁₀ H ₁₆ O | <i>trans</i> -8-Methyl-2-hexahydroindanone | 55.8 |
| C ₁₀ H ₁₈ O ₂ | 2,2,6-Trimethyl-3,5-heptanedione | 55.3 |
| C ₁₀ H ₂₀ O | 2,2,5,5-Tetramethyl-3-hexanone | 46.3 |
| C ₁₁ H ₂₀ O ₂ | 2,2,6,6-Tetramethyl-3,5-heptanedione | 57.1 |
| C ₁₁ H ₂₂ O | Undecanones | 50—65 |
| C ₁₂ H ₂₄ O | 2-Dodecanone | 69.4 |
| CH ₂ O ₂ | Formic acid | 43.8 |
| C ₂ H ₄ O ₂ | Acetic acid | 49.1 |
| C ₃ H ₆ O ₂ | Propionic acid | 52.5 |
| C ₄ H ₈ O ₂ | Butyric acids | 51—56 |
| C ₂ H ₄ O ₂ | Methyl formate | 26 |
| C ₃ H ₆ O ₂ | Esters | 30 |
| C ₄ H ₈ O ₂ | Esters | 33—35 |
| C ₅ H ₈ O ₂ | Methyl cyclopropanecarboxylate | 38.8 |
| C ₇ H ₁₀ O ₂ | Esters | 35—37 |
| C ₈ H ₁₀ O ₂ | Methyl cyclobutanecarboxylate | 42.3 |
| | Ethylene glycol diacetate | 59.0 |
| C ₆ H ₁₂ O ₂ | Esters | 36—41 |
| C ₇ H ₁₄ O ₂ | Esters | 39—46 |
| C ₈ H ₈ O ₂ | Methyl benzoate | 53.1 |
| C ₈ H ₁₄ O ₄ | Ethylene glycol dipropanoate | 65.1 |
| C ₈ H ₁₆ O ₂ | Esters | 49 |
| C ₉ H ₁₄ O ₆ | Triacetin | 83.3 |
| C ₉ H ₁₈ O ₂ | Methyl octanoate | 53.9 |
| C ₁₀ H ₁₈ O ₄ | Ethylene glycol dibutanoate | 70.7 |

TABLE 2 (continued)
Rounded Values of Cohesive Energies at 25°C

| Formula | Compound | $-U/\text{kJ mol}^{-1}$ |
|--|--|-------------------------|
| $\text{C}_{10}\text{H}_{20}\text{O}_2$ | Methyl nonanoate | 59.5 |
| $\text{C}_{11}\text{H}_{22}\text{O}_2$ | Methyl decanoate | 64.3 |
| $\text{C}_{12}\text{H}_{24}\text{O}_6$ | Tripropionin | 88.9 |
| $\text{C}_{12}\text{H}_{24}\text{O}_2$ | Methyl undecanoate | 69.0 |
| $\text{C}_{13}\text{H}_{26}\text{O}_2$ | Methyl dodecanoate | 74.7 |
| $\text{C}_{14}\text{H}_{28}\text{O}_2$ | Methyl tridecanoate | 80.2 |
| $\text{C}_{15}\text{H}_{30}\text{O}_6$ | Glycerol tributryrate | 104.6 |
| $\text{C}_{15}\text{H}_{30}\text{O}_2$ | Methyl tetradecanoate | 84.5 |
| $\text{C}_{16}\text{H}_{32}\text{O}_2$ | Methyl pentadecanoate | 91.0 |
| $\text{C}_2\text{H}_4\text{O}$ | Oxirane, ethylene oxide | 23.0 |
| $\text{C}_3\text{H}_4\text{O}_2$ | β -Propiolactone | 44.6 |
| $\text{C}_3\text{H}_6\text{O}$ | Methyloxirane, propylene oxide | 25.8 |
| | Oxetane, trimethylene oxide | 27.7 |
| $\text{C}_4\text{H}_4\text{O}$ | Furan | 25.2 |
| $\text{C}_4\text{H}_4\text{O}_2$ | Diketene | 40.4 |
| $\text{C}_4\text{H}_8\text{O}$ | Tetrahydropyran | 29.7 |
| $\text{C}_4\text{H}_8\text{O}_2$ | 1,3-Dioxane | 36.7 |
| | 1,4-Dioxane | 36.2 |
| $\text{C}_5\text{H}_{10}\text{O}$ | 3,3-Dimethyloxetane | 31.6 |
| | Tetrahydropyran | 32.2 |
| $\text{C}_5\text{H}_{10}\text{O}_3$ | 1,3,6-Trioxacyclooctane | 46.3 |
| $\text{C}_8\text{H}_{16}\text{O}_4$ | 1,4,7,10-Tetraoxacyclododecane | 63.2 |
| $\text{C}_{10}\text{H}_{20}\text{O}_5$ | 1,4,7,10,13-Pentaoxacyclopentadecane | 77.1 |
| $\text{C}_2\text{H}_5\text{O}_2$ | 2-Methoxyethanol, methyl cellosolve® | 42.7 |
| $\text{C}_4\text{H}_{10}\text{O}_2$ | 2-Ethoxyethanol, cellosolve | 45.8 |
| $\text{C}_3\text{H}_{10}\text{O}_3$ | Diethyl carbonate | 41.1 |
| | 2-Methoxyethyl acetate methyl cellosolve acetate | 47.8 |
| $\text{C}_3\text{H}_{12}\text{O}_2$ | Propoxyethanols | 48—50 |
| $\text{C}_6\text{H}_{12}\text{O}_3$ | 2-Ethoxyethyl acetate cellosolve acetate | 50.2 |
| | Ethoxymethyl propanoate | 47.4 |
| $\text{C}_6\text{H}_{14}\text{O}_2$ | 2-Butoxyethanol, butyl cellosolve | 54.1 |
| $\text{C}_6\text{H}_{14}\text{O}_3$ | 2-Propoxyethyl acetate | 53.1 |
| $\text{C}_8\text{H}_{16}\text{O}_3$ | 2-Butoxyethyl acetate, butyl cellosolve acetate | 57.1 |
| CS_2 | Carbon disulfide | 25.2 |
| $\text{C}_2\text{H}_6\text{S}$ | Dimethyl sulfide | 26.5 |
| $\text{C}_2\text{H}_6\text{S}_2$ | Dimethyl disulfide | 35.4 |
| $\text{C}_3\text{H}_8\text{S}$ | Ethyl methyl sulfide | 29.5 |
| $\text{C}_4\text{H}_{10}\text{S}$ | Methyl propyl sulfide | 33.8 |
| | Isopropyl methyl sulfide | 31.8 |
| | Diethyl sulfide | 33.4 |
| $\text{C}_4\text{H}_{10}\text{S}_2$ | Diethyl disulfide | 42.7 |
| $\text{C}_5\text{H}_{12}\text{S}$ | Dialkyl sulfides | 33—38 |
| $\text{C}_5\text{H}_{12}\text{S}_2$ | Bis(ethylthio)methane | 48.3 |
| $\text{C}_6\text{H}_{14}\text{S}$ | Dialkyl sulfides | 37—43 |
| $\text{C}_6\text{H}_{14}\text{S}_2$ | 1,2-Bis(ethylthio)ethane | 57.0 |
| | Dipropyl disulfide | 56.7 |
| $\text{C}_8\text{H}_{18}\text{S}$ | Dialkyl sulfides | 41—50 |
| $\text{C}_8\text{H}_{18}\text{S}_2$ | Dialkyl disulfides | 52—60 |
| $\text{C}_2\text{H}_6\text{S}$ | Ethanethiol, ethyl mercaptan | 25.1 |
| $\text{C}_2\text{H}_6\text{S}_2$ | 1,2-Ethanedithiol | 42.2 |
| $\text{C}_3\text{H}_8\text{S}$ | Propanethiols | 27—30 |
| $\text{C}_3\text{H}_8\text{S}$ | 1,3-Propanedithiol | 47.2 |
| $\text{C}_4\text{H}_{10}\text{S}$ | 1,4-Butanedithiol | 29—34 |
| $\text{C}_4\text{H}_{10}\text{S}_2$ | Cyclopentanethiol | 39.0 |
| $\text{C}_5\text{H}_{12}\text{S}$ | Pentanethiols | 33—39 |
| $\text{C}_5\text{H}_{12}\text{S}_2$ | 1,5-Pentanedithiol | 56.8 |

TABLE 2 (continued)
Rounded Values of Cohesive Energies at 25°C

| Formula | Compound | $-U/\text{kJ mol}^{-1}$ |
|---|---|-------------------------|
| $\text{C}_6\text{H}_6\text{S}$ | Benzenethiol | 45.1 |
| $\text{C}_6\text{H}_{12}\text{S}$ | Cyclohexanethiol | 42.1 |
| $\text{C}_{10}\text{H}_{22}\text{S}$ | 1-Decanethiol | 63.0 |
| $\text{C}_3\text{H}_6\text{S}$ | Thiacyclobutane | 33.5 |
| $\text{C}_4\text{H}_4\text{S}$ | Thiophene | 32.3 |
| $\text{C}_4\text{H}_6\text{S}$ | Dihydrothiophenes | 35—38 |
| $\text{C}_4\text{H}_8\text{S}$ | Thiacyclopentane | 37.0 |
| $\text{C}_5\text{H}_6\text{S}$ | Methylthiophenes | 36—37 |
| $\text{C}_5\text{H}_{10}\text{S}$ | Thiacyclohexane | 40.1 |
| CN_4O_8 | Tetranitromethane | 47.5 |
| CH_3NO | Formamide | 57.7 |
| CH_3NO_2 | Nitromethane | 35.9 |
| $\text{C}_2\text{H}_5\text{NO}$ | <i>N</i> -Methylformamide | 53.7 |
| $\text{C}_3\text{H}_7\text{NO}$ | <i>N</i> -Ethylformamide | 56.0 |
| | <i>N,N</i> -Dimethylformamide | 44.4 |
| $\text{C}_4\text{H}_9\text{NO}$ | <i>N</i> -Ethylacetamide | 62.4 |
| | <i>N,N</i> -Dimethylacetamide | 47.8 |
| | <i>N</i> -Methylpropionamide | 62.4 |
| | <i>N,N</i> -Diethylformamide | 47.8 |
| $\text{C}_5\text{H}_{11}\text{NO}$ | <i>N</i> -Propylacetamide | 67.3 |
| | <i>N</i> -Isopropylacetamide | 63.9 |
| | <i>N</i> -Methylisobutyramide | 64.6 |
| $\text{C}_6\text{H}_5\text{NO}_2$ | Nitrobenzene | 52.5 |
| $\text{C}_6\text{H}_9\text{NO}_3$ | Triacetamide | 57.9 |
| $\text{C}_6\text{H}_{13}\text{NO}$ | <i>N</i> -Butylacetamide | 72.5 |
| | <i>N,N</i> -Diethylacetamide | 51.6 |
| $\text{C}_6\text{H}_{14}\text{N}_2\text{O}$ | <i>N</i> -Nitrosodipropylamine | 49.2 |
| $\text{C}_8\text{H}_9\text{N}_2\text{O}$ | <i>N</i> -Nitroso- <i>di-tert</i> -butylamine | 43.5 |
| $\text{C}_{10}\text{H}_{17}\text{NO}_2$ | <i>N,N</i> -Diacetylaniline | 68.1 |
| $\text{C}_4\text{H}_8\text{OS}$ | Ethyl thioethanoate | 37.5 |
| $\text{C}_5\text{H}_{10}\text{OS}$ | Propyl thioethanoate | 41.6 |
| | 1-Methylethyl thioethanoate | 39.8 |
| $\text{C}_6\text{H}_{10}\text{OS}$ | Butyl thioethanoate | 45.6 |
| | 1,1-Dimethylethyl thioethanoate | 40.5 |
| $\text{C}_4\text{H}_7\text{NS}$ | 4-Methylthiazole | 41.4 |
| — | Halogen-substituted ethers | 30—52 |
| — | Halogen-substituted esters | 44—49 |
| — | Halogen-substituted diones | 28—35 |

Selected and adapted from Majer, V. and Svoboda, V., *Enthalpy of Vaporization of Organic Compounds*, IUPAC Chemical Data Series No. 32, Blackwell, Oxford, 1985.

limation of solids) and thermodynamics of liquid metal solutions can be discussed in terms of cohesion parameters.^{40,42} Alternative definitions of cohesion parameters for compressed gases are described in Section 11.3.

2.3 THERMODYNAMIC EQUATION OF STATE

Any expression linking the state properties of a material is known as an "equation of state". The most fundamental equation of state is the *thermodynamic equation of state*, which follows from basic thermodynamic relationships and involves pressure p , molar volume v , absolute temperature T , and the molar internal energy U :

TABLE 3
Selected Values of Hildebrand Parameters at 25°C

| Formula | Substance | V/cm ³ mol ⁻¹ | $\Delta_e H$ or $\Delta_m H$ kJ mol ⁻¹ | δ /MPa ^{1/2} |
|-----------------------------------|--|-------------------------------------|---|------------------------------|
| Elements | | | | |
| Br ₂ | Bromine | 51 | 30.7 | 23.5 |
| I ₂ | Iodine | 59 | — | 28.8 |
| S ₈ | Sulfur | 135 | — | 25.4 |
| P ₄ | Phosphorus | 70 | 52.7 | 26.8 |
| Tetrahalides | | | | |
| CCl ₄ | Tetrachloromethane, carbon tetrachloride | 97 | 32.8 | 17.6 |
| SiCl ₄ | Silicon tetrachloride, tetrachlorosilane | 115 | 30.1 | 15.5 |
| SiBr ₄ | Silicon tetrabromide, tetrabromosilane | 127 | 43.4 | 18.0 |
| GeCl ₄ | Germanium tetrachloride | 115 | 33.8 | 16.6 |
| SnCl ₄ | Stannic chloride | 118 | 40.0 | 17.8 |
| SnI ₄ | Stannic iodide | 151 | 82.1 | 23.9 |
| Other Inorganic compounds | | | | |
| OsO ₄ | Osmium tetroxide | 58 | 41.0 | 25.8 |
| MoF ₆ | Molybdenum hexafluoride | 84 | 26.6 | 17.0 |
| WF ₆ | Tungsten hexafluoride | 88 | 26.2 | 16.4 |
| UF ₆ | Uranium hexafluoride | 96 | 30 | 18.2 |
| Si(CH ₃) ₄ | Tetramethylsilane, silicon tetramethyl | 136 | 24.3 | 12.7 |
| Aliphatic Hydrocarbons | | | | |
| C ₅ H ₁₂ | Pentane | 116 | 26.8 | 14.5 |
| | Isopentane, 2-methylbutane | 117 | 25.2 | 13.9 |
| | Neopentane, 2,2-dimethylpropane | 122 | 22.4 | 12.7 |
| C ₆ H ₁₄ | Hexane | 132 | 31.7 | 14.9 |
| C ₇ H ₁₆ | Heptane | 148 | 36.6 | 15.1 |
| C ₈ H ₁₈ | Octane | 164 | 41.5 | 15.3 |
| | Isooctane, 2,2,4-trimethylpentane | 166 | 35.1 | 14.1 |
| | Hexadecane | 294 | 81.1 | 16.4 |
| C ₅ H ₁₀ | Cyclopentane | 95 | 28.7 | 16.6 |
| C ₆ H ₁₂ | Cyclohexane | 109 | 33.1 | 16.8 |
| C ₇ H ₁₄ | Methylcyclohexane | 128 | 35.4 | 16.0 |
| C ₆ H ₁₂ | 1-Hexene | 126 | 30.7 | 14.9 |
| C ₈ H ₁₆ | 1-Octene | 158 | 40.6 | 15.5 |
| C ₆ H ₁₀ | 1,5-Hexadiene | 118 | 31.8 | 15.8 |
| Aromatic Hydrocarbons | | | | |
| C ₆ H ₆ | Benzene | 89 | 33.9 | 18.8 |
| C ₇ H ₈ | Toluene, methylbenzene | 107 | 38.0 | 18.2 |
| C ₈ H ₁₀ | Ethylbenzene | 123 | 42.3 | 18.0 |
| | <i>o</i> -Xylene, 1,2-dimethylbenzene | 121 | 43.4 | 18.4 |
| | <i>m</i> -Xylene, 1,3-dimethylbenzene | 123 | 42.7 | 18.0 |
| | <i>p</i> -Xylene, 1,4-dimethylbenzene | 124 | 42.4 | 18.0 |
| | Propylbenzene | 140 | 46.2 | 17.6 |
| C ₉ H ₁₂ | Mesitylene, 1,3,5-trimethylbenzene | 140 | 47.5 | 18.0 |
| | Styrene, ethenylbenzene | 116 | 43.9 | 19.0 |
| C ₁₀ H ₈ | Naphthalene | 123 | — | 20.3 |
| C ₁₄ H ₁₀ | Anthracene | (150) | — | 20.3 |
| | Phenanthrene | 158 | — | 20.0 |

TABLE 3 (continued)
Selected Values of Hildebrand Parameters at 25°C

| $\delta/\text{MPa}^{1/2}$ | Formula | Substance | $V/\text{cm}^3 \text{ mol}^{-1}$ | Δ_{H} or $\Delta_{\text{L}} H$ kJ mol ⁻¹ | $\delta/\text{MPa}^{1/2}$ |
|--|---|---|----------------------------------|--|---------------------------|
| Fluorocarbons | | | | | |
| 23.5 | C ₆ F ₁₄ | Perfluorohexane | 205 | 32.4 | 12.1 |
| 28.8 | C ₇ F ₁₆ | Perfluoroheptane | 226 | 36.4 | 12.3 |
| 25.4 | C ₆ F ₁₂ | Perfluorocyclohexane | 170 | 28.9 | 12.5 |
| 26.8 | C ₇ F ₁₄ | Perfluoro(methylcyclohexane) | 196 | 33.1 | 12.5 |
| Other Fluorochemicals | | | | | |
| 17.6 | (C ₄ F ₉) ₃ N | Perfluorotributylamine | 360 | 54.4 | 12.7 |
| 15.5 | C ₄ Cl ₂ F ₆ | Dichlorohexafluorocyclobutane | 142 | — | 14.5 |
| 18.0 | C ₄ Cl ₃ F ₇ | 2,2,3-Trichloroheptafluorobutane | 165 | 35.6 | 14.1 |
| 16.6 | C ₂ Cl ₃ F ₃ | 1,1,2-Trichloro-1,2,2-trifluoroethane | 120 | 27.5 | 14.5 |
| 17.8 | C ₇ F ₁₅ H | Pentadecafluoroheptane | 215 | 37.7 | 12.9 |
| 23.9 | | | | | |
| Other Aliphatic Halogen Compounds | | | | | |
| 25.8 | CH ₂ Cl ₂ | Dichloromethane, methylene dichloride | 64 | 28.6 | 20.0 |
| 17.0 | CHCl ₃ | Trichloromethane, chloroform | 81 | 31.0 | 18.8 |
| 16.4 | CCl ₄ | Tetrachloromethane, carbon tetrachloride | 97 | 32.8 | 17.6 |
| 18.2 | CHBr ₃ | Tribromomethane, bromoform | 88 | 43.1 | 21.5 |
| 12.7 | CHI ₃ | Iodomethane, methyl iodide | 63 | 28.0 | 20.3 |
| | CH ₂ I ₂ | Diiodomethane, methylene diiodide | 81 | — | 24.1 |
| | C ₂ H ₅ Cl | Chloroethane, ethyl chloride | 74 | 23.8 | 17.0 |
| | C ₂ H ₅ Br | Bromoethane, ethyl bromide | 75 | 27.2 | 18.2 |
| | C ₂ H ₅ I | Iodethane, ethyl iodide | 81 | 32.2 | 19.2 |
| 14.5 | C ₂ H ₄ Cl ₂ | 1,2-Dichloroethane, ethylene dichloride | 79 | 34.7 | 20.3 |
| 13.9 | | 1,1-Dichloroethane, ethylidene dichloride | 85 | 32.2 | 18.6 |
| 12.7 | C ₂ H ₄ Br ₂ | 1,2-Dibromoethane, ethylene dibromide | 90 | 41.4 | 20.9 |
| 14.9 | C ₂ H ₃ Cl ₃ | 1,1,1-Trichloroethane | 100 | 32.6 | 17.4 |
| 15.1 | C ₂ H ₂ Cl ₂ | <i>cis</i> -1,2-Dichloroethylene | 76 | 28.9 | 18.6 |
| 15.3 | | <i>trans</i> -1,2-Dichloroethylene | 78 | 28.5 | 18.4 |
| 14.1 | C ₂ Cl ₄ | Tetrachloroethylene | 103 | 39.7 | 19.0 |
| 16.4 | | | | | |
| 16.6 | | | | | |
| 16.8 | | | | | |
| 16.0 | | | | | |
| 14.9 | CS ₂ | Carbon disulfide | 61 | 28.0 | 20.5 |
| 15.5 | C ₃ H ₈ O ₂ | Dimethoxymethane, methylal | 89 | 27.6 | 16.8 |
| 15.8 | C ₄ H ₁₀ O | Diethyl ether | 105 | 26.6 | 15.1 |

Adapted from Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L., *Regular and Related Solutions*, van Nostrand-Reinhold, Princeton, NJ, 1970.

$$(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$$

Many liquids have values of $(\partial p/\partial T)_V$ and $(\partial U/\partial V)_T$ which are functions only of the molar volume within experimental precision over reasonably wide temperature and pressure ranges.^{15,16} Because they show this simple behavior, these functions have been given special names and symbols. The *internal pressure* is

$$\pi \equiv (\partial U/\partial V)_T \tag{8a}$$

and the isochoric (constant volume) *thermal pressure coefficient* is

TABLE 3a
Molar Volumes and Hildebrand Parameters
of Dichloro-Substituted *n*-Alkanes at 25°C

| | V/cm ³ mol ⁻¹ | δ/MPa ^{1/2} |
|----------------------|-------------------------------------|----------------------|
| 1,1-Dichloroethane | 84.8 | 18.3 |
| 1,1-Dichloropropane | 100.5 | 18.0 |
| 1,1-Dichlorobutane | 116.9 | 17.8 |
| 1,1-Dichloropentane | 133.8 | 17.9 |
| 1,1-Dichlorohexane | 150.7 | 17.8 |
| 1,1-Dichloroheptane | 167.3 | 17.8 |
| 1,1-Dichlorooctane | 183.6 | 17.8 |
| 1,1-Dichlorononane | 199.2 | 17.7 |
| 1,1-Dichloroundecane | 233.2 | 17.6 |
| 1,2-Dichloroethane | 79.4 | 20.3 |
| 1,2-Dichloropropane | 98.2 | 18.5 |
| 1,2-Dichlorobutane | 114.3 | 18.0 |
| 1,2-Dichloropentane | 131.2 | 17.8 |
| 1,2-Dichlorohexane | 148.1 | 17.6 |
| 1,2-Dichloroheptane | 164.4 | 17.8 |
| 1,2-Dichlorooctane | 181.2 | 17.8 |
| 1,2-Dichlorononane | 197.9 | 17.7 |
| 1,2-Dichloroundecane | 232.0 | 17.6 |
| 1,3-Dichloropropane | 95.8 | 20.0 |
| 1,4-Dichlorobutane | 112.1 | 19.8 |
| 1,5-Dichloropentane | 128.7 | 19.4 |
| 1,6-Dichlorohexane | 145.9 | 19.7 |
| 1,7-Dichloroheptane | 162.6 | 19.6 |
| 1,8-Dichlorooctane | 179.5 | 19.6 |
| 1,10-Dichlorodecane | 213.2 | 19.4 |
| 2,2-Dichloropropane | 104.2 | 16.9 |

$$\beta \equiv (\partial p / \partial T)_V \quad (9a)$$

Thus, Equation 7 can be written

$$\pi = T\beta - p \quad (8b)$$

The thermal pressure coefficient β is related to the isothermal compressibility κ and the thermal expansion coefficient α by

$$\beta = \alpha / \kappa \quad (9b)$$

and from Equation 7, neglecting p , which is usually much smaller than the other term,

$$\pi = T\beta = T\alpha / \kappa \quad (10)$$

The internal pressure results from the forces of attraction between molecules in condensed phases exceeding the forces of repulsion, and although there is obviously a close connection between internal pressure and cohesive pressure, they are not equivalent: the cohesive pressure c is a measure of the total molecular cohesion per unit volume (an integral quantity), while the internal pressure π is the instantaneous isothermal volume derivative of the internal energy (a differential quantity). The expression

$$\pi = nc \quad (11)$$

TABLE 4
Cohesion Parameters and Atomic Volumes of the Elements

| Element | Atomic number | Atomic volume cm ³ mol ⁻¹ | $[(\Delta H - RT)/V]^{1/2}$ MPa ^{1/2} | T/K |
|------------|---------------|--|---|-----|
| Actinium | 39 | 22.6 | 139 | 298 |
| Aluminum | 13 | 10 | 180 | 298 |
| Antimony | 51 | 18.2 | 119 | 298 |
| Argon | 18 | 23.9 | 16 | 28 |
| Arsenic | 33 | 13.1 | 149 | 28 |
| Astatine | 85 | * | * | — |
| Barium | 56 | 39.2 | 57 | 298 |
| Beryllium | 4 | 4.4 | 258 | 298 |
| Bismuth | 83 | 21.3 | 99 | 298 |
| Boron | 5 | 4.7 | 346 | 298 |
| Bromine | 35 | (25.5) | 66 | 298 |
| Cadmium | 48 | 13.0 | 93 | 298 |
| Calcium | 20 | 26.0 | 83 | 298 |
| Carbon | 6 | 5.3 | 366 | 298 |
| Cerium | 58 | 20.7 | 141 | 298 |
| Cesium | 55 | 70.1 | 34 | 298 |
| Chlorine | 17 | (19.3) | 79 | 298 |
| Chromium | 24 | 7.2 | 235 | 298 |
| Cobalt | 27 | 6.7 | 253 | 298 |
| Copper | 29 | 7.1 | 219 | 298 |
| Dysprosium | 66 | 19.0 | 121 | 298 |
| Erbium | 68 | 13.3 | 127 | 298 |
| Europium | 63 | 29.0 | 78 | 298 |
| Fluorine | 9 | (10.3) | 88 | 298 |
| Francium | 87 | 73.0 | 32 | 298 |
| Gadolinium | 64 | 20.0 | 131 | 298 |
| Gallium | 31 | 11.8 | 152 | 298 |
| Germanium | 32 | 13.6 | 166 | 298 |
| Gold | 79 | 10.2 | 190 | 298 |
| Hafnium | 72 | 13.6 | 227 | 298 |
| Helium | 2 | 19.5 | 2.2 | 1 |
| Holmium | 67 | 18.8 | 125 | 298 |
| Hydrogen | 1 | (6.7) | 254 | 298 |
| Indium | 49 | 15.7 | 124 | 298 |
| Iodine | 53 | (25.7) | 64 | 298 |
| Iridium | 77 | 8.5 | 279 | 298 |
| Iron | 26 | 7.1 | 243 | 298 |
| Krypton | 36 | 32.0 | 17 | 121 |
| Lanthanum | 57 | 22.4 | 138 | 298 |
| Lead | 82 | 18.3 | 104 | 298 |
| Lithium | 3 | 13.0 | 112 | 298 |
| Lutetium | 71 | 17.8 | 153 | 298 |
| Magnesium | 12 | 14.0 | 103 | 298 |
| Manganese | 25 | 7.4 | 196 | 298 |
| Mercury | 80 | 14.8 | 64 | 298 |
| Molybdenum | 42 | 9.4 | 265 | 298 |
| Neodymium | 60 | 20.6 | 124 | 298 |
| Neon | 10 | 16.8 | 11 | 24 |
| Nickel | 28 | 6.6 | 255 | 298 |
| Niobium | 41 | 10.8 | 260 | 298 |
| Nitrogen | 7 | (11.4) | 203 | 298 |
| Osmium | 76 | 8.4 | 305 | 298 |
| Oxygen | 8 | (8.5) | 171 | 298 |
| Palladium | 46 | 8.9 | 206 | 298 |
| Phosphorus | 15 | 16.9 | 139 | 298 |

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TABLE 4 (continued)
Cohesion Parameters and Atomic Volumes of the Elements

| Element | Atomic number | Atomic volume cm ³ mol ⁻¹ | $[(\Delta H - RT)/V]^{1/2}$ MPa ^{1/2} | T/K |
|---------------|---------------|--|---|-----|
| Platinum | 78 | 9.1 | 249 | 298 |
| Polonium | 84 | 22.6 | 80 | 298 |
| Potassium | 19 | 45.5 | 45 | 298 |
| Praseodymium | 59 | 20.8 | 131 | 298 |
| Promethium | 61 | 20.3 | 115 | 298 |
| Protoactinium | 91 | 15.0 | 192 | 298 |
| Radium | 88 | 38.8 | 67 | 298 |
| Radon | 86 | 50.5 | 60 | 208 |
| Rhenium | 75 | 8.9 | 297 | 298 |
| Rhodium | 45 | 8.3 | 259 | 298 |
| Rubidium | 37 | 55.9 | 38 | 298 |
| Ruthenium | 44 | 8.3 | 279 | 298 |
| Samarium | 62 | 20.1 | 102 | 298 |
| Scandium | 21 | 15.1 | 150 | 298 |
| Selenium | 34 | 16.5 | 112 | 298 |
| Silicon | 14 | 12.1 | 194 | 298 |
| Silver | 47 | 10.3 | 167 | 298 |
| Sodium | 11 | 23.7 | 68 | 298 |
| Strontium | 38 | 33.7 | 70 | 298 |
| Sulfur | 16 | 15.5 | 134 | 298 |
| Tantalum | 73 | 10.9 | 267 | 298 |
| Technetium | 43 | 8.6 | 273 | 298 |
| Tellurium | 52 | 20.5 | 98 | 298 |
| Terbium | 64 | 19.3 | 140 | 298 |
| Thallium | 81 | 17.3 | 102 | 298 |
| Thorium | 90 | 19.9 | 170 | 298 |
| Thulium | 69 | 18.2 | 116 | 298 |
| Tin | 50 | 16.3 | 136 | 298 |
| Titanium | 22 | 10.6 | 211 | 298 |
| Tungsten | 74 | 9.5 | 296 | 298 |
| Uranium | 92 | 12.5 | 205 | 298 |
| Vanadium | 23 | 8.4 | 248 | 298 |
| Xenon | 54 | 36.8 | 19 | 166 |
| Ytterbium | 70 | 24.9 | 82 | 298 |
| Yttrium | 39 | 19.9 | 144 | 298 |
| Zinc | 30 | 9.2 | 120 | 298 |
| Zirconium | 40 | 14.1 | 208 | 298 |

^a No data available.

Adapted from Lawson, D. D., *Proc., DOE Chemical/Hydrogen Energy Contractor Review Systems*, CONF-771131, National Technical Information Service, Springfield, VA, 1978, 109. See also Tables 24 and 25, Chapters 5, for liquid metals.

with n an empirical parameter can be used (see next section). Although n approaches a value of unity for nonpolar liquids, it can be considerably less than or greater than unity for other liquids, as shown in Table 12, Chapter 7.

The internal pressure π is in some ways a more satisfactory quantity than the cohesive pressure c or the Hildebrand parameter ($\delta = c^{1/2}$) to describe the macroscopic resultant of molecular interactions. This is because π is defined thermodynamically and because it may be evaluated directly and unambiguously in some situations. The effects on reaction kinetics and other properties of change in solvent internal pressure parallel those resulting from external pressure variation, and are experimentally simpler to achieve.¹⁷ The relationship

between π and c is considered in more detail in Section 7.5, where the internal pressure is shown to provide one method of estimating the Hildebrand parameter values for simple liquids, and component cohesion parameters for more complex liquids. Sharma and Das¹⁸⁻²¹ and Wilson^{22,23} are among those who have considered various aspects of equations of state, cohesion parameters, and internal pressure.

2.4 EMPIRICAL EQUATIONS OF STATE

In the course of numerous attempts to analyze and rationalize the nature of intermolecular forces, many empirical equations of state have been proposed. The most used equation, of course, is the ideal gas law,

$$pV = RT \quad (12)$$

but the next best known is the van der Waals equation of state²⁴⁻²⁶

$$(p + a/V^2)(V - b) = RT \quad (13)$$

The thermodynamic equation of state (Equation 7) and the van der Waals equation can be rewritten as follows to yield a direct comparison:

$$p + (\partial U/\partial V)_T = T(\partial p/\partial T)_V \quad (14)$$

$$p + a/V^2 = TR/(V - b) \quad (15)$$

It is then possible to define a *van der Waals liquid* as one that obeys the equation

$$(\partial U/\partial V)_T = a/V^2 \quad (16)$$

Integrating,

$$U = -a/V^2 \quad (17)$$

If $U = -\Delta_g U$ (Equation 3), then

$$a = V\Delta_g U = V^2 c = V^2 \delta^2 \quad (18)$$

and

$$(\partial U/\partial V)_T = \Delta_g U/V = c = \delta^2 \quad (19)$$

This very simple relationship between the Hildebrand parameter and van der Waals a parameter has been shown approximately true for some liquids.^{8-10,27-29} More generally,³⁰⁻³²

$$U = -a/V^n \quad (20)$$

which, with the assumption that the vapor is ideal, leads to

$$(\partial U/\partial V)_T = n(\Delta_g U/V) \quad (21)$$

so the deviation of n from unity (Table 12, Chapter 7) can be used as a measure of the extent of deviation of a real liquid from a van der Waals liquid.

McGowan³³ classified three main types of property (or combination of properties) for liquids:

- Those which are constant for all unassociated liquids, such as the characteristic pressure, p_x (4455 MPa)
- Those (most properties) which vary with temperature
- Those which vary between compounds but which do not depend on temperature, such as the parachor (Section 6.3) and also the van der Waals a and b parameters

The estimation of both the parameters a and b and cohesion parameters from characteristic atomic volumes and characteristic pressure was discussed.

Equations of state are considered further in Chapter 7.

2.5 UNITS AND CONVERSION FACTORS

The internal pressure is expressed in pressure units (preferably in the SI unit, the pascal, $1 \text{ Pa} \equiv 1 \text{ N m}^{-2}$), but in the past the cohesive pressure or cohesive energy density has been given units of energy per unit volume, often cal cm^{-3} . As internal pressure and cohesive pressure are dimensionally identical, it is logical to use a common unit. Also, although the units cal cm^{-3} for cohesive pressure and $\text{cal}^{1/2} \text{ cm}^{-3/2}$ for solubility parameters are still used widely, eventual conversion to the SI units is inevitable, and these units are used throughout this book. It is not now appropriate to honor the founder of the solubility parameter concept by adopting the "hildebrand" as the title of the non-SI unit $\text{cal}^{1/2} \text{ cm}^{-3/2}$ as originally suggested by Taylor,³⁴ and a more permanent form of recognition is desirable. This is achieved by calling the original thermodynamic or "total" cohesion parameter, as defined in Equation 5 or 6, the *Hildebrand parameter*.

From many points of view, the most appropriate and convenient unit for cohesion parameters is $\text{MPa}^{1/2}$, which is numerically identical with $\text{J}^{1/2} \text{ cm}^{-3/2}$ and with $\text{MJ}^{1/2} \text{ m}^{-3/2}$. This conforms to the SI conventions, is of convenient numerical size ($1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ being approximately $2 \text{ MPa}^{1/2}$), and can be written in compact form. Tables 5 and 6 list some conversion factors for pressure units and for cohesion parameter units.

In Chapter 6 the quantity $(-UV)^{1/2}$ is introduced, with dimensions

$$(\text{energy})^{1/2} (\text{volume})^{1/2} (\text{amount})^{-1} \equiv (\text{pressure})^{1/2} (\text{volume}) (\text{amount})^{-1}$$

and the conversion to SI units is

$$\begin{aligned} (\text{energy})^{1/2} (\text{volume})^{1/2} (\text{amount})^{-1} &\equiv (\text{pressure})^{1/2} (\text{volume}) (\text{amount})^{-1} \\ 1 \text{ cal}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1} &= 2.0455 \text{ J}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1} (\text{MPa}^{1/2} \text{ cm}^3 \text{ mol}^{-1}) \end{aligned}$$

In Chapter 7, dimensionless coefficients have been converted from $\text{cal}^{1/2} \text{ cm}^{-3/2} \text{ atm}^{-1/2}$ using

$$1 \text{ cal}^{1/2} \text{ cm}^{-3/2} \text{ atm}^{-1/2} = 6.4260$$

and the parameter $A = \delta^2 V^{1/3} \gamma^{-1}$ in Chapter 17 has been converted to $\text{mol}^{-1/3}$ from $\text{cal erg}^{-1} \text{ mol}^{-1/3}$ by using 4.184×10^7 as a multiplying factor. In Chapter 6, for the normal lyoparachor and true lyoparachor,

$$1 \text{ cal}^{4/5} \text{ g}^{-4/5} \text{ cm}^3 \text{ mol}^{-1} = 3.143 \text{ J}^{4/5} \text{ g}^{-4/5} \text{ cm}^3 \text{ mol}^{-1}$$

$$1 \text{ cal}^{3/4} \text{ g}^{-3/4} \text{ cm}^3 \text{ mol}^{-1} = 2.925 \text{ J}^{3/4} \text{ g}^{-3/4} \text{ cm}^3 \text{ mol}^{-1}$$

The dipole moment is frequently quoted in the non-SI debye unit,

TABLE 5
Pressure Units and Conversion Factors

| | cal cm ⁻³ | MPa (J cm ⁻³) | atm | bar | kg cm ⁻² | mmHg (0°C) |
|-----------------------------|----------------------|------------------------------|--------------|--------------|---------------------|---------------|
| 1 cal cm ⁻³ | — | 4.184 0 | 41.292 9 | 41.840 | 42.665 | 31 383 |
| 1 MPa (J cm ⁻³) | 0.239 01 | — | 9.869 2 | 10.000 | 10.197 2 | 7 500.6 |
| 1 atm | 0.024 217 | 0.101 325 | — | 1.013 25 | 1.033 23 | 760.00 |
| 1 bar | 0.023 901 | 0.100 000 | 0.986 92 | — | 1.019 72 | 750.06 |
| 1 kg cm ⁻² | 0.023 439 | 0.098 066 | 0.967 84 | 0.9806 | — | 735.56 |
| 1 mmHg (0°C) | 0.000 031 865 | 0.000 133 322 | 0.001 315 78 | 0.001 332 22 | 0.001 359 5 | — |

TABLE 6
Cohesion Parameter Units and Conversion Factors

| | cal ^{1/2} cm ^{-3/2} | MPa ^{1/2} (J ^{1/2} cm ^{-3/2}) | atm ^{1/2} |
|--|---------------------------------------|--|--------------------|
| 1 cal ^{1/2} cm ^{-3/2} | — | 2.045 5 | 6.4260 |
| 1 MPa ^{1/2} (J ^{1/2} cm ^{-3/2}) | 0.488 88 | — | 3.1415 |
| 1 atm ^{1/2} | 0.155 62 | 0.318 32 | — |

$$1 D = 3.336 \times 10^{-30} C m$$

Density conversions are made using

$$1 \text{ lb (US gal)}^{-1} = 0.11983 \text{ g cm}^{-3}$$

2.6 MIXTURES

For mixing to be possible, the Gibbs free energy of mixing at constant pressure must be negative:

$$\Delta_m G_p = \Delta_m H_p - T\Delta_m S_p < 0 \quad (22)$$

The entropy change $\Delta_m S_p$, of a mixing process is usually positive, but in order to predict if mixing will take place, it is necessary to evaluate the enthalpy term, $\Delta_m H_p$. When this term is negative, or positive and less than $T\Delta_m S_p$, mixing can occur. Because of the temperature dependence of the entropy term, if the temperature of a mixture is decreased spontaneous "unmixing" (phase separation) may occur, although it is also possible for metastable homogeneous systems to exist.

Through thermodynamic relationships, cohesion parameters can also provide information on the properties of the components within mixtures. Differentiation of the Gibbs free energy of mixing with respect to the amount of substance i provides the chemical potential ${}^i\mu^\circ$ in the pure liquid. The chemical potential is also known as the relative partial molar Gibbs free energy, or the Gibbs free energy of dilution, and can be subdivided into enthalpy of dilution and entropy of dilution terms. The activity, ${}^i a$, of component i follows from

$$RT \ln {}^i a = {}^i\mu - {}^i\mu^\circ \quad (23)$$

The usual approach to the study of thermodynamic properties of mixtures or solutions is to determine the changes in the values of certain characteristic properties when the components

are mixed. In doing this, the concept of an *ideal mixture* or *ideal solution* is valuable in describing the idealized behavior of mixtures, as in the same way the ideal gas law describes the idealized, limiting behavior of expanded gases. It is demonstrated in most general physical chemistry textbooks that the thermodynamic definition of an ideal mixture (a mixture in which the activity equals the mole fraction composition over the entire composition range and over a nonzero range of temperature and pressure) leads to the following properties:

1. There is *no volume change* during the formation of an ideal mixture from its components, $\Delta_m V = 0$. (The volume change on mixing can be determined experimentally by dilatometry.)
2. There is *no enthalpy change* in the system when the components are mixed at a fixed total pressure; that is, there is a zero heat of mixing, $\Delta_m H = 0$. (Experimentally, there would be no temperature change observed in a thermally isolated system during an ideal mixing process.)
3. There is an *entropy change* during mixing equal to that occurring during the formation of an ideal gas mixture due to the extra degrees of freedom created by the mixing process. This is sometimes called the combinatorial entropy, and for equal-sized, low molecular mass components the molar entropy of mixing is

$$\Delta_m S = -R \sum_i x_i \ln x_i \quad (24)$$

where x_i is the mole fraction of component i . (Each mole fraction x_i is less than unity, so $\ln x_i$ is negative and the overall $\Delta_m S$ term is positive.) Different relative molecular sizes of the components reduce the number of possible combinations, and $\Delta_m S$ is less than the ideal value (Section 13.2).

4. The resulting molar *Gibbs free energy change* during the formation of an ideal mixture is therefore completely provided by the entropy gained by each component:

$$\Delta_m G = \Delta_m H - T\Delta_m S = RT \sum_i x_i \ln x_i \quad (25)$$

5. The components forming an ideal mixture are always *completely miscible* in all proportions.

Another way of considering an ideal mixture is on the molecular level: an ideal mixture is one in which the different types of molecules, i and j for example, behave exactly as if they were surrounded by molecules of their own kind; that is, all intermolecular interactions are equivalent. This is discussed further below.

In *nonideal mixtures*, the Gibbs free energy change for the mixing process is not equal to the ideal value, and the "excess" Gibbs free energy change on mixing is³⁵

$${}^E\Delta_m G = \Delta_m G - RT \sum_i x_i \ln x_i \quad (26)$$

This function may be considered either from the point of view of the mixed *system* as the excess G^E of the Gibbs free energy of the nonideal mixture relative to that of the ideal mixture, or from the point of view of the mixing *process* as the excess ${}^E\Delta_m G$ of the nonideal Gibbs free energy of mixing relative to the ideal Gibbs free energy of mixing.¹⁰ Similarly, the excess entropy of mixing is defined

$${}^E\Delta_m S = \Delta_m S + R (x_1 \ln x_1 + x_2 \ln x_2) \quad (27)$$

An ideal mixture follows *Raoult's law*, which states that the partial pressure, p_i , of any component i is given by

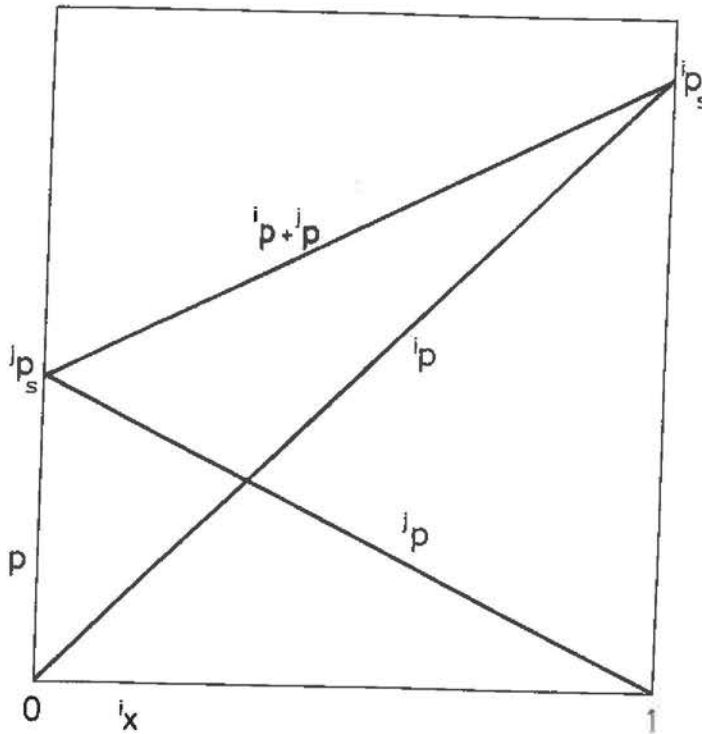


FIGURE 1. Total and partial vapor pressures in an ideal binary mixture at constant temperature.

$$^i p = ^i x p_s^i \tag{28}$$

where $^i x$ is the mole fraction of component i in the mixture and p_s^i is the saturation pressure of component i . This ideal behavior is illustrated in Figure 1. A real system with behavior close to ideal is tetrachloromethane-cyclohexane.

Negative deviations from Raoult's law (Figure 2) occur when interactions between unlike molecules ($i - j$ interactions) are markedly stronger than like-pair interactions. *Moderate positive deviations* (Figure 3) are usual, and occur when there is little or no specific interaction between any of the molecules. *Strong positive deviations* result from situations where molecules of one or more of the components undergo strong self-interaction, but only normal interactions with other components, as in alcohol-hydrocarbon mixtures. *Very strong positive deviations* from Raoult's law lead to liquid-liquid immiscibility (Section 2.7).

Nonideality is also frequently described in terms of activity coefficients. Except for the special case of an ideal mixture, the activity a_i of component i is not equal to its mole fraction value $^i x$, and it is therefore convenient to define the activity coefficient f_x^i such that

$$f_x^i = a_i / ^i x \tag{29}$$

The Gibbs free energy change on mixing is then expressed

$$\Delta_m G = RT \sum_i ^i x \ln ^i x + RT \sum_i ^i x \ln a_i = \ln ^i x + RT \sum_i ^i x \ln f_x^i \tag{30}$$

and from Equation 26,

$$^E \Delta_m G = RT \sum_i ^i x \ln f_x^i \tag{31}$$

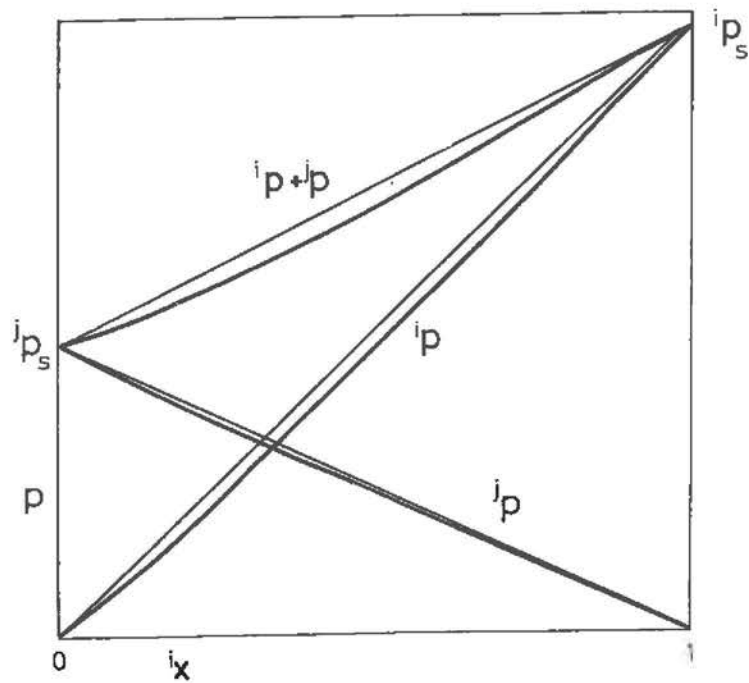


FIGURE 2. Total and partial vapor pressures at constant temperature for a system with negative deviations from Raoult's law.

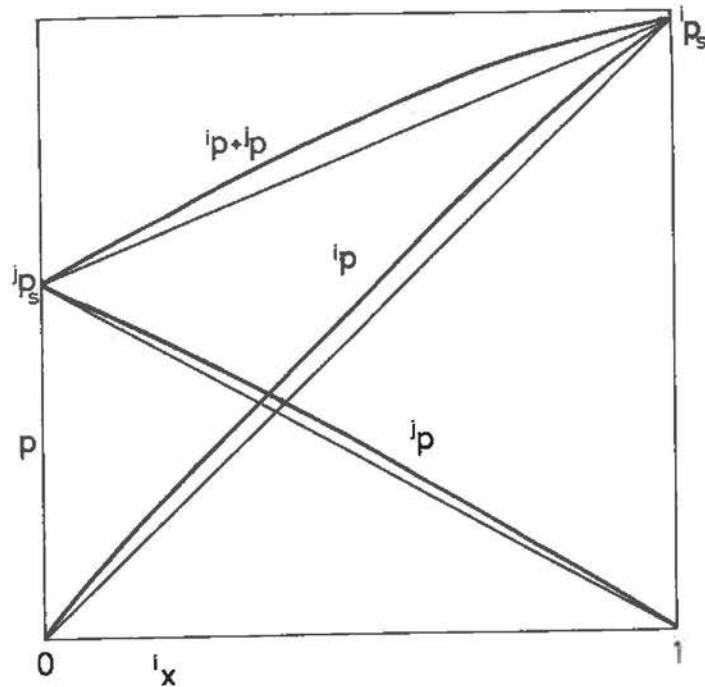


FIGURE 3. Total and partial vapor pressures at constant temperature for a system with moderate positive deviations from Raoult's law.

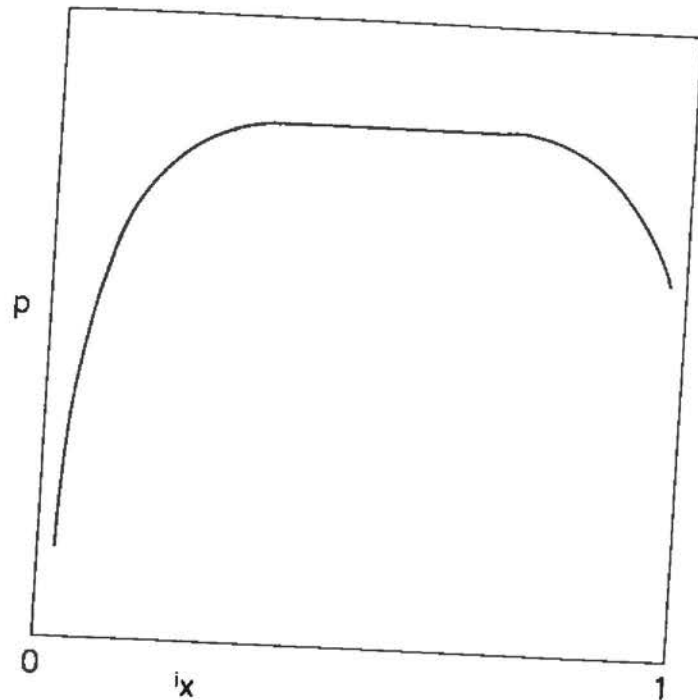


FIGURE 4. Total vapor pressure in equilibrium with a partially miscible pair of liquids, at constant temperature.

Hildebrand's definition^{36,37} of a *regular solution* arises from the separation of the Gibbs free energy of mixing at constant pressure into entropy and enthalpy components (Equation 22): "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." In other words, a solution of mixture described as "regular" is one which, despite a nonideal (nonzero, either positive or negative) 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 $i-j$ interactions which differ from the original $i-i$ and $j-j$ interactions. The concept has proven valuable in the development of an understanding of miscibility criteria and of deviations from ideality. Unfortunately, although the term "regular solution" has come into general use, the usage does not always conform with its original definition.³⁸ The definition in terms of an ideal entropy of mixing forms the most useful reference state and should be retained. When molecules of different sizes are mixed, an alternative entropy of mixing term is required, as described subsequently (Section 13.2).

2.7 PHASE SEPARATION

It was stated in the previous section that when there are strong self-interactions in the components of a mixture and weaker interactions between components, there occur strong positive deviations from Raoult's law which can lead to liquid-liquid immiscibility. In Figure 4, which can be compared with Figures 1 to 3, the flat portion of the pressure-composition curve represents the miscibility gap.

The possibility of this type of behavior can be investigated in an alternative way by plotting the excess Gibbs free energy of mixing (Equation 26) against the mole fraction.³⁹ If this curve has no point of inflexion and is concave upward (Figure 5a), the binary mixture

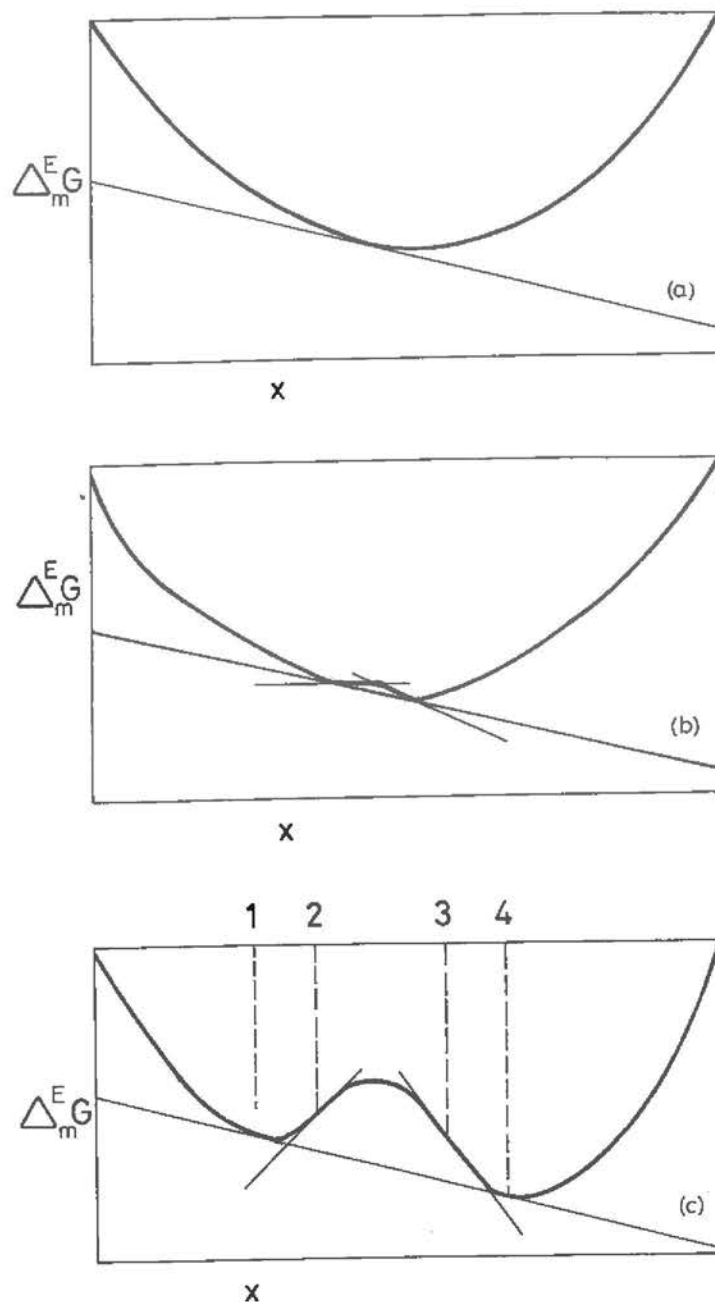


FIGURE 5. Excess Gibbs free energy of a binary mixture as a function of mole fraction: (a) miscibility in all proportions; (b) onset of demixing; (c) existence of two regions of stability, two regions of metastability, and one region of instability. (Adapted from Dayantis, J., *Plast. Mod. Elastomers*, 29(2), 58, 1977.)

is stable at all compositions and no phase separation occurs. If the curve has two upward-facing concavities separated by a convex section and two points of inflexion (Figure 5c), there is a region of total instability, two metastable regions and, at either end of the composition range, two regions of binary mixture stability. An attempt to obtain a mixture with a composition between points 2 and 3 leads to two phases with compositions represented by points 2 and 4 defined by the double tangent to the curve. Curve 5b is the limiting case, defining a critical miscibility situation where the two points of inflexion coincide. As the temperature of some liquid-liquid systems is decreased, the behavior may be represented by each of Figures 5a, b, and c in turn as complete miscibility at higher temperatures changes to phase separation at lower temperatures. The temperature corresponding to diagram (b) is then called the (upper) critical solution temperature, UCST. Polymer-liquid, polymer-polymer systems (Section 13.3) and a very few liquid-liquid systems, like aqueous amine solutions, exhibit a second critical solution temperature as the temperature of the mixture is raised.

It should also be noted that useful polymer-polymer and polymer-liquid dispersions and metastable solutions can be produced from thermodynamically incompatible systems if the ingredients can be mixed in the appropriate thermodynamic conditions and then prevented from demixing when the conditions are changed (Chapter 16).

REFERENCES

1. Polak, J., Heat of vaporization and cohesion energy of liquids, *Collect. Czech. Chem. Comm.*, 31, 1483, 1966.
2. Majer, V., Svoboda, V., Pošta, A., and Pick, J., Enthalpy data of liquids. XXII. Determination of heats of vaporization and some other thermodynamic quantities for three fluorinated halogen ethanes, *Collect. Czech. Chem. Commun.*, 46, 817, 1981.
3. Svoboda, V., Charvatova, V., Majer, V., and Pick, J., Enthalpy data on liquids. XXIV. Determination of heats of vaporization and other thermodynamic quantities for four alkylcycloparaffins, *Collect. Czech. Chem. Commun.*, 46, 2983, 1981.
4. Svoboda, V., Cohesion energy of liquids, *Chem. Listy*, 76, 389, 1982.
5. Uchytílová, V., Majer, V., and Svoboda, V., Enthalpies of vaporization and cohesive energies of 2-chloro-1,1,2-trifluoroethyl ethyl ether, 2-chloro-1,1,2-trifluoroethyl propyl ether, 2-chloro-1,2-trifluoroethyl chloromethyl ether and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether, *J. Chem. Thermodyn.*, 16, 475, 1984.
6. Majer, V., Svoboda, V., and Lencka, M., Enthalpies of vaporization and cohesive energies of pyridine and isomeric methylpyridines, *J. Chem. Thermodyn.*, 16, 1019, 1984.
7. Majer, V. and Svoboda, V., *Enthalpies of Vaporization of Organic Compounds*, IUPAC Chemical Data Series No. 32, Blackwell, Oxford, 1985.
8. Hildebrand, J. H. and Scott, R. L., *Solubility of Non-Electrolytes*, 3rd ed., Reinhold, New York, 1950; Dover, New York, 1964.
9. Hildebrand, J. H. and Scott, R. L., *Regular Solutions*, Prentice-Hall, Englewood Cliffs, NJ, 1962.
10. Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L., *Regular and Related Solutions*, Van Nostrand-Reinhold, Princeton, NJ, 1970.
11. Teas, J. P., Re solubility parameters, *J. Paint Technol.*, 40, 104, 1968.
12. Gardon, J. L. and Teas, J. P., Solubility parameters, in *Treatise on Coatings*, Vol. 2, Part II, Myers, R. R. and Long, J. S., Eds., Marcel Dekker, New York, 1976, chap. 8, 413.
13. Lawson, D. D., Applications of solubility parameters. Part I, *Proc. DOE Chemical/Hydrogen Energy Contractor Review Systems*, (Pasadena, CA, 1977), CONF-771131, National Technical Information Service, Springfield, VA, 1978, 109.
14. England, C., Lawson, D. D., and Hrubec, J. D., Superconductivity, cohesive energy density, and electron-atom ratio in metals, *J. Appl. Phys.* 52, 2923, 1981.
15. Barton, A. F. M., Internal pressure. A fundamental liquid property, *J. Chem. Educ.*, 48, 156, 1971.
16. Barton, A. F. M., *The Dynamic Liquid State*, Longman, London, 1974.
17. Ouellette, R. J. and Williams, S. H., Internal solvent pressure. I. A demonstration of the effect of internal solvent pressure on conformational equilibria, *J. Am. Chem. Soc.*, 93, 466, 1971.

18. Sharma, B. K., A new method of estimation of solubility parameter of liquids, *Indian J. Pure Appl. Phys.*, 124, 939, 1976; Solubility parameter and evaluation of some thermodynamic properties of simple liquids, *Indian J. Pure Appl. Phys.*, 15, 633, 1977.
19. Sharma, B. K., Internal pressure-temperature behaviour and lattice Gruncisen constant of polymers, *Acustica*, 48, 121, 1981.
20. Sharma, B. K., Statistical thermodynamics of liquids. I. An equation of state and solubility parameter, *Acustica*, 49, 164, 1981.
21. Sharma, B. K. and Das, N., Internal pressure-temperature behavior and solubility parameter of liquids, *Indian J. Pure Appl. Phys.*, 19, 668, 1981.
22. Wilson, G. M., Interpretation of Trouton's law, solubility parameters, molecular size and polarity in relation to equation of state properties, *Abs. Pap. Am. Chem. Soc.*, 189, (Apr.), 110, 1985.
23. Wilson, G. M., Interpretation of Trouton's law in relation to equation of state properties, *Am. Chem. Soc. Symp. Ser.*, 300, (Equations of State), 520, 1986.
24. Del Rio, F., Guzman, F., and Mier y Teran, L., The van der Waals model and the theory of solutions, *Chem. Phys. Lett.*, 35, 274, 1975.
25. Haward, R. N., Modified van der Waals equation for liquids, *Trans. Faraday Soc.*, 62, 828, 1966.
26. Rowlinson, J. S., Legacy of van der Waals, *Nature (London)*, 224, 414, 1973.
27. Hildebrand, J. H., Compressibilities and thermal pressure coefficients of certain liquids, *Phys. Rev.*, 34, 649, 1929.
28. Hildebrand, J. H., *Solubility of Non-Electrolytes*, 2nd ed., Reinhold, New York, 1936; (Russian translation), Gonti, Moscow-Leningrad, 1938.
29. Hildebrand, J. H. and Carter, J. M., A study of van der Waals forces between tetrahalide molecules, *J. Am. Chem. Soc.*, 54, 3592, 1932.
30. Frank, H. S., Free volume and entropy in condensed systems. II. Liquids, *J. Chem. Phys.* 13, 493, 1945.
31. Fried, V. and Schmeier, G. B., Some comments on cohesion energies of liquids, *J. Phys. Chem.*, 72, 4688, 1968.
32. Amoras, J., Solana, J. R., and Villar, E., Behaviour of the internal pressure of liquids in accordance with variations in temperature, volume and cohesive energy density, *Mater. Chem. Phys.*, 10, 557, 1984.
33. McGowan, J. C., The estimation of solubility parameters and related properties of liquids, *J. Chem. Tech. Biotechnol.*, 34A, 38, 1984.
34. Taylor, N. W., in *Modern Chemistry for the Engineer and Scientist*, Robertson, G. R., Ed., McGraw-Hill, New York, 1957, p 183.
35. Eckert, C. A., Introduction to theories of solutions and application to phase equilibria, in *Solutions and Solubilities*, Part II, Dack, M. R. J., Ed., John Wiley & Sons-Interscience, New York, 1976, chap. 9.
36. Hildebrand, J. H., Solubility. XII. Regular solutions, *J. Am. Chem. Soc.*, 51, 66, 1929.
37. Hildebrand, J. H., Order from chaos, *Science*, 150, 441, 1965.
38. Hildebrand, J. H., The term 'regular solution,' *Nature (London)*, 168, 868, 1951.
39. Dayantis, J., The Hildebrand parameter. Solubility of polymers, *Plast. Mod. Elastomers*, 29(2), 58, 1977.
40. Bowersox, D. F., Thermodynamic properties of selected solutes in liquid metal solutions, *U.S.A.E.C.*, CONF-690801, 565-75, 1969.
41. Varushchenko, R. M., Loseva, O. L., and Druzhinina, A. I., Energies of evaporation of dichloroalkanes, *Zh. Fiz. Khim.*, 62, 2329, 1988; *Russ. J. Phys. Chem.*, 62, 1204, 1988.
42. Yatsenko, S. P. and Dieva, G. N., Solubility of high-melting metals in molten indium, *Zh. Fiz. Khim.*, 47, 2948, 1973; *Russ. J. Phys. Chem.*, 47, 1658, 1973.

REGULAR SOLUTIONS AND THE HILDEBRAND PARAMETER

The Hildebrand parameter developed from regular solution theory, but whereas a regular solution is an idealized concept (a mixture in which the partial excess entropy is zero), the Hildebrand parameter, the geometric mean approximation, and the component cohesion parameters to be introduced in the next chapter are general concepts. These originated in regular solutions, but also can be applied to varying extents of other types of solution. This distinction is important, but is not always made.

4.1 GEOMETRIC MEAN APPROXIMATION

As introduced in Section 2.6, a regular solution has an ideal entropy of formation, arising from a completely random molecular distribution, despite the existence of interactions which lead to a nonideal (non-zero) enthalpy of formation. This effectively restricts regular mixtures to those systems in which only dispersion forces are important, because the orientation effects of polar molecules cause nonrandom molecular distributions. The extent of the dispersion effect depends on the ionization potential and the polarizability of the molecules concerned (Equation 6, Chapter 3). Ionization potentials, I , and intermolecular distances, r , do not usually vary greatly for different pairs of adjacent molecules, and to a good approximation

$$I + I \approx 2(IJ)^{1/2} \quad (1)$$

and

$$r \approx 2(r'r)^{1/2} \quad (2)$$

This forms the basis of the geometric mean relation for dispersion interactions,

$$\bar{U}_d = {}^iU_d^{1/2} {}^jU_d^{1/2} \quad (3)$$

which is a major approximation in cohesion parameter theory. Early in the development of the cohesion parameter concept, the geometric mean approximation was tested experimentally on eight mixtures of tetrahalomethanes. Hildebrand and Carter¹ verified to within 1% the relationship

$$\bar{U}_d = ({}^i x {}^i a^{1/2} + {}^j x {}^j a^{1/2})^2 \quad (4)$$

where $a = TV^2\beta$ (Equations 10 and 16, Chapter 2) for the mixture $i-j$ and the components i and j , which would follow from

$$\bar{U}_d = {}^i x^2 {}^i a + {}^j x^2 {}^j a + 2{}^i x {}^j x \bar{U}_d \quad (4a)$$

if $\bar{U}_d = ({}^i a^j)^{1/2}$. Further tests were made by Scatchard et al.² and Staveley et al.³, and the geometric mean approximation can be considered to be justified, at least in favorable circumstances, although discussion on its validity continues⁴⁻⁹. Empirical correction methods for deviations are described in Section 5.7.

4.2 HILDEBRAND-SCATCHARD EQUATION

The regular solution equation for the internal energy of mixing at constant volume, based

on the pioneering work of van der Waals¹⁰ and van Laar,^{11,12} was derived on semitheoretical grounds by Scatchard^{13,14} and Hildebrand¹⁵⁻¹⁹ and popularized by J. H. Hildebrand, R. L. Scott, J. M. Prausnitz, and others.²⁰⁻³⁵

The energy of mixing for 1 mol of solution is

$$\Delta_m U_v = ({}^i x {}^i V + {}^j x {}^j V) {}^i j A {}^i \phi {}^j \phi \quad (5)$$

$$= {}^i V ({}^i x + m {}^j x) {}^i j A {}^i \phi {}^j \phi \quad (6)$$

In these equations, x is the mole fraction, V is the molar volume, m is the ratio of molar volumes, and ϕ is the volume fraction:

$$m = {}^j V / {}^i V = (M^j / M^i) (\rho^i / \rho^j) \quad (7)$$

$${}^i \phi = {}^i V {}^i x / ({}^i V {}^i x + {}^j V {}^j x) = {}^i x / (m {}^j x + {}^i x) \quad (8)$$

$${}^j \phi = {}^j V {}^j x / ({}^i V {}^i x + {}^j V {}^j x) = m {}^j x / (m {}^j x + {}^i x) \quad (9)$$

The superscripts i and j identify the components of the binary mixture, i being the solvent and j the solute if this distinction is made. ${}^i j A$ is a measure of the change of the cohesion pressure or energy density associated with the i - j mixing process, called the *exchange energy density* or *exchange cohesive pressure*, and given by

$${}^i j A = {}^i c + {}^j c - 2 {}^i j c \quad (10)$$

where the ${}^i c$ term is the cohesive pressure characteristic of the intermolecular forces acting between molecules of type i and j . This equation can be appreciated in a simple fashion by considering what happens when unit volumes of components i and j are mixed: two i - j interactions are formed for each pair of i - i and j - j interactions broken. It should be noted that ${}^i j A$ is not simply the difference between the cohesive pressure of components i and j ; this quantity (${}^i c - {}^j c$) has been termed³⁶ the "mutual cohesion factor", but has not proved of great value in correlating the properties of materials.

The interchange cohesive pressure ${}^i j A$ can be used simply as an empirical parameter for a particular i - j pair of series of mixtures, like the physical interaction parameter of Harris and Prausnitz,³⁷ but this does not make full use of the opportunity to develop a method to provide information on *mixtures* from data on individual *components*. This is where the relationship between ${}^i j A$ and the individual Hildebrand parameters ${}^i \delta$ and ${}^j \delta$ is important.

The Hildebrand parameters for the substances are defined by Equation 5, Chapter 2, so

$${}^i \delta^2 = {}^i c = \Delta^i U / V \quad \text{and} \quad {}^j \delta^2 = {}^j c = \Delta^j U / V \quad (11)$$

Using the geometric mean approximation, Equation 3,

$${}^i j c = ({}^i c {}^j c)^{1/2} \quad (12)$$

so

$$\begin{aligned} {}^i j A &= ({}^i c^{1/2} - {}^j c^{1/2})^2 = ({}^i \delta - {}^j \delta)^2 \\ &= {}^i \delta^2 + {}^j \delta^2 - 2 {}^i j c \end{aligned} \quad (13)$$

and the Hildebrand-Scatchard equation can be written

$$\begin{aligned}\Delta_m U_v &= ({}^i x {}^i V + {}^j x {}^j V) {}^i A {}^i \phi {}^j \phi \\ &= ({}^i x {}^i V + {}^j x {}^j V) ({}^i \delta - {}^j \delta)^2 {}^i \phi {}^j \phi\end{aligned}\quad (14)$$

This provides the basis of the cohesion parameter approach to liquid miscibility and other properties. The Hildebrand-Scatchard equation, although a very simple predictive relationship, is still proving useful.⁸⁸⁻⁹¹

One of the most important derived properties is the activity coefficient. The partial molar energy of transfer of component j is obtained by differentiating Equation 5 with respect to the amount of j , and assuming an ideal entropy of transfer, the resulting expression for the activity coefficient⁹ is

$$RT \ln {}^j f_x = RT \ln ({}^j a^j/x) = {}^j V {}^i \phi^2 {}^i A = {}^j V {}^i \phi^2 ({}^i \delta - {}^j \delta)^2 \quad (15)$$

Similarly,

$$RT \ln {}^i f_x = RT \ln ({}^i a^i/x) = {}^i V {}^j \phi^2 {}^j A = {}^i V {}^j \phi^2 ({}^i \delta - {}^j \delta)^2 \quad (15a)$$

Expanding Equation 15,

$$RT \ln {}^j f_x = {}^j V [({}^i V {}^i x) / ({}^i V {}^j \alpha + {}^i V {}^i x)]^2 ({}^i \delta - {}^j \delta)^2 \quad (15b)$$

In dilute solutions, ${}^j V X \ll {}^i V X$, and in infinitely dilute solutions ${}^i \phi = 1$, so

$$RT \ln {}^j f_x^\infty = {}^j V {}^i A = {}^j V ({}^i \delta - {}^j \delta)^2 \quad (16)$$

A more general expression for the limiting infinite dilution activity coefficient of component j with molar volume ${}^j V$ in a multicomponent mixture is

$$RT \ln {}^j f_x^\infty = {}^j V ({}^i \delta - \bar{\delta})^2 \quad (17)$$

where $\bar{\delta}$ is the volume fraction average Hildebrand parameter (Equation 41). If the i and j molecules differ appreciably in size, inclusion of the Flory-Huggins size effect term is necessary (Section 13.2). This involves replacing $-R \ln {}^i x$ in the entropy of mixing with

$$-R [\ln {}^i \phi + {}^j \phi (1 - {}^i V/V)]$$

and leads to

$$RT \ln {}^j f_x = {}^j V {}^i \phi^2 {}^i A + RT [\ln {}^i \phi/x + {}^j \phi (1 - {}^i V/V)] \quad (18)$$

or

$$\ln {}^i a = {}^i V {}^j \phi^2 {}^j A / (RT) + \ln {}^i \phi + {}^j \phi (1 - {}^i V/V) \quad (19)$$

For solute j ,

$$RT \ln {}^j f_x = {}^j V {}^i \phi^2 {}^i A + RT [\ln {}^j \phi/x + {}^i \phi (1 - {}^j V/V)] \quad (20)$$

and for infinitely dilute solutions of j in i where ${}^i \phi = 1$ and ${}^j \phi/x = {}^j V/V$,

$$RT \ln f_x^\infty = {}^jV u_A + RT[\ln({}^jV/{}^iV) + 1 - {}^jV/{}^iV] \quad (21)$$

or

$$\ln f_x^\infty = {}^jV/(RT) u_A + {}^j d \quad (21a)$$

where the Flory-Huggins combinatorial size effect term is

$${}^j d = \ln({}^jV/{}^iV) + 1 - {}^jV/{}^iV \quad (21b)$$

The upper critical solution temperature, UCST, (Section 2.7) for an i - j mixture can be found from the Gibbs free energy of mixing (excess term plus ideal term: see Section 2.6),

$$\Delta_m G = {}^E\Delta_m G + {}^I\Delta_m G = RT ({}^i x \ln {}^i x f_x + {}^j x \ln {}^j x f_x) \quad (22)$$

Insertion of the Hildebrand-Scatchard expression for a binary mixture gives

$$\Delta_m G/(RT) = ({}^i x {}^iV + {}^j x {}^jV) u_A \phi^i \phi^j + {}^i x \ln {}^i x + {}^j x \ln {}^j x \quad (23)$$

$$\Delta_m G/(RT) = [{}^i x {}^j x {}^iV {}^jV ({}^i\delta - {}^j\delta)^2]/({}^i x {}^iV + {}^j x {}^jV) + {}^i x \ln {}^i x + {}^j x \ln {}^j x \quad (23a)$$

The second and third derivatives of the Gibbs free energy of mixing with respect to mole fraction are set equal to zero, corresponding to the situation illustrated in Figure 5b, Chapter 2, and the simultaneous solution yields

$${}^i x = [{}^iV - ({}^iV^2 + {}^jV^2 - {}^iV {}^jV)^{1/2}]/({}^iV - {}^jV) \quad (24)$$

$$T_{cs} = 2{}^i x {}^j x {}^iV^2 {}^jV^2 u_A / [R({}^i x {}^iV + {}^j x {}^jV)^2] \quad (25)$$

or

$$T_{cs} = 2{}^i x {}^j x {}^iV^2 {}^jV^2 ({}^i\delta - {}^j\delta)^2 / [R({}^i x {}^iV + {}^j x {}^jV)^2] \quad (25a)$$

If the molar volumes are close in value, ${}^iV = {}^jV$, and

$$T_{cs} = V({}^i\delta - {}^j\delta)^2 / (2R) \quad (26)$$

The relationships between T_{cs} and δ for hydrocarbons and film-forming materials have been explored by Mandik³⁸. The rest of the liquid (1)-liquid (2) phase boundary can also be determined, with the equations

$$RT \ln(x_1/x_2) = {}^jV ({}^i\phi_2^2 - {}^j\phi_1^2)({}^i\delta - {}^j\delta)^2 \quad (27)$$

$$RT \ln({}^i x_1/{}^j x_2) = {}^iV ({}^i\phi_2^2 - {}^j\phi_1^2)({}^i\delta - {}^j\delta)^2 \quad (27a)$$

or by means of the corresponding equations with u_A replacing $({}^i\delta - {}^j\delta)^2$. The experimental UCST may be used to evaluate u_A , which is then used to generate the whole phase boundary curve. In partially miscible systems, dispersion forces usually dominate over polar and specific effects, and the regular solution model is usually a good approximation.

If Flory-Huggins entropy is substituted for ideal mixing entropy, the corresponding expression for the critical solution temperature is

$$(21) \quad T_{cs} = 2 \text{ }^i v \text{ }^i A \text{ }^i V \text{ }^i V / (V^{1/2} + \text{ }^i V^{1/2})^2$$

or

$$(21a) \quad T_{cs} = 2 (\text{ }^i \delta - \text{ }^j \delta)^2 \text{ }^i V \text{ }^j V / (V^{1/2} + \text{ }^i V^{1/2})^2 \quad (28)$$

For the situation of the limiting miscibility of component j (such as water) in component i (such as a low permittivity organic liquid), where the high- j (organic) solution can be considered to be in equilibrium with pure i (water), it is possible to derive an expression for the solubility of j in i (water in the organic phase). If $f_x = f^\circ$, Equation 21 can be written in terms of the mole fraction solubility of j in i , x_s (solubility of water in the organic phase):

$$(22) \quad -RT \ln x_s = \text{ }^i V \text{ }^i A + RT(\ln \text{ }^i V | \text{ }^i V + 1 - \text{ }^i V | \text{ }^i V) \quad (29)$$

If $\text{ }^i V \approx \text{ }^i V$,

$$(23) \quad -RT \ln x_s = \text{ }^i V \text{ }^i A \quad (29a)$$

The interchange cohesive pressure $\text{ }^i A$ may be expanded, (Equation 13),

$$(23a) \quad \text{ }^i A = \text{ }^i \delta^2 + \text{ }^j \delta^2 - 2\text{ }^i u_c$$

and the value of $\text{ }^i u_c$ can be used as a measure of the degree of interaction or liquid-liquid (water-organic, for example) complexing.³⁹ Equation 29a further simplifies with the geometric mean approximation to

$$(24) \quad -RT \ln x_s = \text{ }^i V (\text{ }^i \delta - \text{ }^j \delta)^2 \quad (30)$$

$$(25) \quad -RT \ln x_s = \text{ }^i V (\text{ }^i \delta - \text{ }^j \delta)^2 \quad (30a)$$

as used in early studies.⁴⁰

4.3 LIMITATIONS OF THE HILDEBRAND-SCATCHARD EQUATION

It should be noted that the Hildebrand-Scatchard equation provides an expression in terms of the constant volume internal energy of mixing, not the constant pressure enthalpy of mixing which is the quantity usually measured in experimental determinations. Although these are identical if there is no volume change on mixing, the effect of volume changes,⁴¹ which are particularly significant at high temperatures, is to produce a disparity between $\Delta_m U_v$ and $\Delta_m H_p$ which is typically of the same order of magnitude as $\Delta_m U_v$.⁴²

In the opinion of the author, the Hildebrand-Scatchard expression and the equations derived from it are best considered as relatively simple semi-empirical equations that have sufficient theoretical foundation on a molecular level to work reasonably well, so no formal derivation is provided here. Accounts emphasizing physical significance and making comparisons with other liquid theories have been published.⁴³⁻⁴⁸ Several modifications incorporate polar and association effects (Chapter 5).

It is instructive to summarize the assumptions made in the original derivation as they highlight the strengths and weaknesses of the resulting equation:

1. It is assumed that the interaction forces act between the *centers* of the molecules.
2. It is assumed that the interactions are *additive*: the interaction between a pair of molecules is not influenced by the presence of other molecules.

3. It is assumed that the mixing is *random*, with neither $i-j$, $j-j$, nor $i-j$ nearest neighbor situations being favored, and the distribution is temperature independent.
4. The constant pressure change of volume on mixing is assumed *zero* with the numbers of nearest neighbors of a molecule in the mixture and in the pure state being considered to be the same.
5. The *geometric mean approximation*, Equation 12, already has been discussed.

These assumptions are not, of course, generally valid, but they produce an equation which has proven valuable both in its own right and as a starting point for other empirical expressions.

Entropy factors are not taken into account in regular solution theory, but when cohesion parameters are used to define the limits of solubility (which corresponds to $\Delta_m G_p$ in Equation 22, Chapter 2, being equal to zero), it follows that $\Delta_m H_p = T\Delta_m S_p$, and entropy is an inherent part of the resulting prediction.⁴⁹ In order to establish phase conditions, Gibbs free energies or chemical potentials must be evaluated. Lee⁴⁵ has developed "irregular solution theory" by incorporating "hard convex body" entropic effects, and has carried out numerical calculations for binary mixtures (Section 7.6).

As well as the theoretical shortcomings, there is a computational problem with cohesion parameters due to the lack of accurate data. Bagley and Scigliano⁴² have demonstrated this in the case of a mixture of two typical organic liquids, both with $V = 100 \text{ cm}^3 \text{ mol}^{-1}$, but with ΔU values of 3.3 and 3.8 mol^{-1} . If the ΔU value used for the first component is only 5% too high, the correct $\Delta_m U_v$ would be 100% higher. Variations of several percent in reported values of vaporization energies are not unusual, even for common solvents. Another assumption implicit in the Hildebrand-Scatchard equation is that the quantity $(-UV)^{1/2}$ is additive. Not only does this quantity appear to be additive in many systems on a solute-solvent basis, but also to a considerable extent for atoms or groups of atoms within molecules. These additive constants, named group molar attraction constants (Section 6.4), are of considerable value in the estimation of cohesion parameters.

An interesting extension⁵⁰⁻⁵² of the Hildebrand-Scatchard equations assumes that the intermolecular forces between polyatomic molecules are not of a central type but peripheral in nature, so it is possible to refer the intermolecular potential energy or cohesion energy to the surface of the molecules and to derive a "surface" modification of the Hildebrand-Scatchard equation. Although it has been claimed that this method is more widely applicable than the original, correlations have not been studied extensively so far.

4.4 MIXED LIQUIDS AND MULTICOMPONENT SYSTEMS

Practical good solvents may be blends of poor solvents or even of nonsolvents,⁹² and it is therefore important to be able to evaluate the effective cohesion parameters of liquid mixtures. Although other factors such as viscosity, volatility, and cost must also be considered in solvent formulation, the effective cohesion parameters are particularly valuable.

For ternary systems, an example of the simplest Hildebrand parameter approach is the prediction that for three phases to coexist

$$|\delta - \delta|/\text{MPa}^{1/2} \leq 5 \leq |\delta - \delta|/\text{MPa}^{1/2}$$

as observed for diamyl ether-acetonitrile-glycerol.⁵³ In a few cases, vaporization enthalpies (1,4-dioxane-water,⁵⁴ hexane-cyclohexanone⁵⁵) or condensation enthalpies (trichloromethane-acetone, trichloromethane-ether⁵⁶) of binary mixtures have been determined experimentally, but usually it is necessary to evaluate cohesion parameters from the properties of the pure components. Mixed solvents are commonly encountered in polymer systems (Section

16.6), and in this connection Table 9 of Chapter 8 contains Hildebrand parameters of various liquid mixtures. Binary liquids are also of pharmaceutical importance, and cohesion parameters have been used extensively for this purpose by Martin and co-workers.⁵⁷⁻⁶² (See also Sections 5.7 and 12.2.)

On the basis of the assumptions made in the derivation of cohesion parameter expressions,²⁹ the effective Hildebrand parameter $\bar{\delta}$ of a binary liquid mixture is

$$\bar{\delta} = (\phi^i \delta^i + \phi^j \delta^j) / (\phi^i + \phi^j) \quad (31)$$

where ϕ is the volume fraction (Equation 8), predicting that the effective Hildebrand parameter of a mixture is volume-wise proportional to the Hildebrand parameters of its components. When the value of the Hildebrand parameter ${}^k\delta$ of solute k in the mixed solvent lies between the Hildebrand parameters δ^i and δ^j of the two component liquids, the solute should be completely miscible when the ratio ϕ^i/ϕ^j is adjusted so that ${}^k\delta = \bar{\delta}$, even if liquids i and j individually are nonsolvents for k .

By definition, the volume fractions must total unity,

$$\phi^i + \phi^j + \phi^k = 1$$

so if ϕ^k is small,

and

$$\bar{\delta} = \phi^i \delta^i + \phi^j \delta^j \quad (32)$$

As a special case, if $V^i \approx V^j$,

$$\bar{\delta} \approx x^i \delta^i + x^j \delta^j \quad (32a)$$

The more general expression for the effective Hildebrand parameter is

$$\bar{\delta} = \sum_i \phi^i \delta^i / \sum_i \phi^i \quad (32b)$$

It is of interest that the critical solution temperatures have been shown (for the hydrocarbon-aniline systems) also to be additive on a volume fraction basis:⁶²

$$\bar{T}_{cs} = \sum_i T_{cs}^i \phi^i$$

Equation 32 has been found to give excellent results in predicting the properties of C_4 and C_5 hydrocarbon vapor-liquid systems (Section 11.5) and the solubilities of gases in mixtures of benzene and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) (Section 11.2), but this equation is not always quantitatively accurate.⁶³ 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 or more nonsolvents. An example of this "cosolvency"⁶⁴ is diethyl ether ($\delta = 15.1 \text{ MPa}^{1/2}$) and ethanol ($\delta = 26.0 \text{ MPa}^{1/2}$) as a solvent mixture for cellulose nitrate ($\delta = 23 \text{ MPa}^{1/2}$). However, frequently when the solute solubility (kx_s) is plotted against $\bar{\delta}$ (a curve which by regular solution theory should be a parabola, as indicated in Section 12.1), asymmetrical curves are observed, with the maximum value of kx_s not appearing at ${}^k\delta$ and the maximum being lower than ideal. For example, the solubility of 2-nitro-5-methylphenol (${}^k\delta = 21.9 \text{ MPa}^{1/2}$) is shown in Figure 1 for two binary liquid systems, cyclohexane-diiodomethane and ethanol-hexane. Also, it is possible for the "solvent power" of a mixture to be less than that of its components, a phenomenon which has been called "cononsolvency".⁶⁵

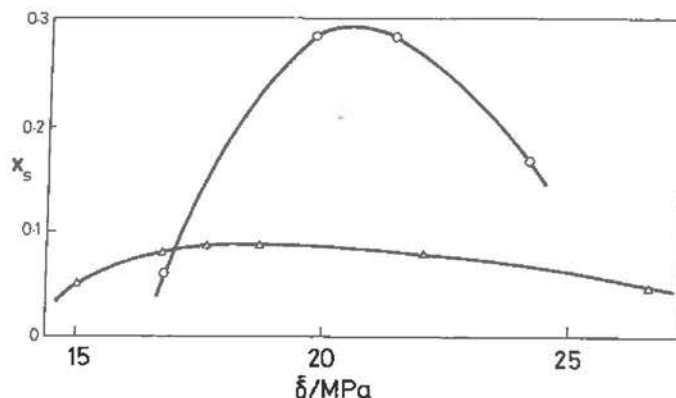


FIGURE 1. Variation in the solubility of 2-nitro-5-methylphenol as a function of the effective Hildebrand parameter of the binary solvent mixtures cyclohexane-diiodomethane (O) and ethanol-hexane (Δ) at 25°C. (Adapted from Buchowski, H., Domanska, U., and Ksiazczak, A., *Pol. J. Chem.*, 53, 1127, 1979.)

The relations between Hamaker constants, originally developed in a microscopic model for adhesion^{66,67} for bodies of materials i and j embedded in medium k are of interest in connection with this, showing on the basis of the geometric mean rule that the interaction of two different materials with a third medium in which they are immersed can be stronger than the interaction between the materials themselves, so spontaneous separation can occur as a result of dispersion forces only.

Purkayastha and Walkley⁶⁸ attempted to improve on Equation 32 by defining an effective volume fraction, ϕ^* , which reflects the preferential "solvation" by one of the liquid components:

$$\bar{\delta} = {}^i\delta \phi^* + {}^j\delta \phi^* \quad (33)$$

In those cases where $k\phi$ is small, then

$${}^i\phi^* + {}^j\phi^* = 1 \quad (33a)$$

and the effective volume fractions are related to the true volume fractions ϕ by

$${}^i\phi^*/\phi^* = [{}^i\phi({}^k\delta - {}^j\delta)^2]/[{}^j\phi({}^k\delta - {}^i\delta)^2] \quad (34)$$

In other words, the effective volume fractions are themselves related to the bulk volume fractions in terms of the Hildebrand parameters, in such a way that they are inversely proportional to the ratios of the enthalpies of mixing of the solute k in each of the pure solvents i and j . An alternative equation based on Christian's⁶⁹ idea of a Boltzmann factor in the enthalpy of complex formation was proposed by Nakanishi and Asakura⁷⁰ for iodine in mixed liquids. Other approaches to the problem of complex formation in solution are discussed in section 7.9.

More generally, for a multicomponent mixture²⁹ the excess Gibbs free energy of mixing is

$${}^E\Delta_m G = (\sum_i {}^i x {}^i V)({}^1/2 \sum_i \sum_j {}^i A {}^j \phi) + RT \sum_i {}^i x \ln ({}^i \phi / {}^i x) \quad (35)$$

where ${}^i A = {}^j A$ and ${}^i A = {}^j A = 0$. The second term is the Flory-Huggins correction for size effect (Section 13.2), but if ${}^i x = {}^i \phi$ for every component, that is if

$${}^iV = {}^jV = {}^kV \dots$$

then

$${}^E\Delta_m G = (\sum_i {}^i x_i {}^i V) (1/2 \sum_i \sum_j {}^i A_i {}^j \phi_i {}^j \phi_j) \tag{36}$$

The activity coefficient of component *n* is obtained from the partial derivative (constant *T*, *p*, and *i* for *i* ≠ *k*)

$$RT \ln({}^k a_i / {}^k x_i) = RT \ln {}^k f_x = [(\partial {}^i n {}^E \Delta_m G) / \partial {}^k n] \tag{37}$$

where *i**n* is the amount of substance *i* and *n* is the total amount of substance. This can be shown to be

$$RT \ln {}^k f_x = {}^k V \sum_i \sum_j ({}^k A_{ij} - 1/2 {}^i A_j) {}^i \phi_j {}^j \phi_i + RT [\ln ({}^k \phi_i / {}^k x_i) + 1 - {}^k \phi_i / {}^k x_i] \tag{38}$$

Only if *i**x* = *i**φ* for all *i* does this equation reduce to

$$RT \ln {}^k f_x = {}^k V \sum_i \sum_j ({}^k A_{ij} - 1/2 {}^i A_j) {}^i \phi_j {}^j \phi_i \tag{39}$$

and with Equation 13,

$$RT \ln {}^k f_x = {}^k V ({}^k \delta - \bar{\delta})^2 \tag{40}$$

where the effective Hildebrand parameter of the mixture is

$$\bar{\delta} = \sum_i {}^i \phi_i {}^i \delta_i \tag{41}$$

the summation extending over all components, including the solute *k* when the volume fraction *i**φ* is appreciable.

There has been considerable discussion on the prediction of optimum solvent mixtures for polymers (Section 16.6), and Hansen parameters have proven very convenient for representation as three-dimensional vectors (Section 14.5). The vector representation was introduced by Froehling, Koenhen, Bantjes, and Smolders,⁷¹ this was improved by Rigbi⁷² and by Froehling and Hillegers.⁷³ Behnken⁷⁴ extended the analysis to the problem of finding the best solvent mixtures with any number of components by means of readily available multiple regression programs. The only requirement is that the program should permit fitting the general equation

$$y = b_1 x_1 + b_2 x_2 + \dots = b_k x_k \tag{42}$$

without a leading constant term, and the input variables needed for the computer can be calculated by hand from the Hansen parameters of the polymer and liquid components.

Equations incorporating experimentally determined composition dependence of vaporization enthalpy may be used⁷⁵ for calculating the Hildebrand parameter of binary liquid mixtures in an extension of the methods described in Section 7.2.

4.5 SOLVENT SPECTRA

A list of liquids may be compiled with gradually increasing Hildebrand parameter values

TABLE 1
Liquids for Hildebrand Parameter
Spectra, Divided According to Hydrogen-
Bonding Capability

Liquids with Poor Hydrogen-Bonding Capability

| | |
|---------------------------------|------|
| Pentane | 14.3 |
| Heptane | 15.1 |
| Methylcyclohexane | 16.0 |
| Solvesso® 150 | 17.4 |
| Toluene | 18.2 |
| Tetrahydronaphthalene, tetralin | 19.4 |
| <i>o</i> -Dichlorobenzene | 20.5 |
| 1-Bromonaphthalene | 21.7 |
| Nitroethane | 22.7 |
| Acetonitrile | 24.1 |
| Nitromethane | 26.0 |

Liquids with Moderate Hydrogen-Bonding
Capability

| | |
|------------------------|------|
| Diethyl ether | 15.1 |
| Diisobutyl ketone | 16.0 |
| Butyl acetate | 17.4 |
| Methyl propionate | 18.2 |
| Dibutyl phthalate | 19.0 |
| 1,4-Dioxane | 20.3 |
| Dimethyl phthalate | 21.9 |
| 2,3-Butylene carbonate | 24.8 |
| Propylene carbonate | 27.2 |
| Ethylene carbonate | 30.1 |

Liquids with Strong Hydrogen-Bonding Capability

| | |
|---|------|
| 2-Ethylhexanol | 19.4 |
| Methyl isobutyl carbinol, 1,2-dimethyl- propanol | 20.5 |
| 2-Ethylbutanol | 21.5 |
| 1-Pentanol | 22.3 |
| 1-Butanol | 23.3 |
| 1-Propanol | 24.3 |
| Ethanol | 26.0 |
| Methanol | 29.7 |

Adapted from Burrell, H., *Polymer Handbook*, Brandrup, J. and Immergut, E. H., Eds., John Wiley & Sons, New York, 1966, IV—341 and 1975, IV—337.

to form a "solvent spectrum"^{64,76-83} In its most common form (Table 1), it includes subdivision into categories of hydrogen-bonding ability. The Hildebrand parameter of a solute is taken as the midpoint of the range of liquid Hildebrand parameters which provides complete miscibility. "Fine control" over liquid Hildebrand parameter values can be provided using mixtures of liquids, the effective Hildebrand parameter of a mixture being calculated by Equation 31, or to some extent by changing the temperature. The ASTM D3121 test method for polymer solubility ranges (Table 9, Chapter 8) uses liquid mixtures to provide a spectrum of closely spaced Hildebrand parameters. For polymers (section 14.3), either the dissolution behavior of a polymer or the swelling of a slightly cross-linked analog of the polymer of

TABLE 2
Hildebrand Parameters and Molar Volumes
for Cholesterol and Triglycerides

| | | $\delta/\text{MPa}^{1/2}$ | $V/\text{cm}^3 \text{ mol}^{-1}$ |
|--------------|-------|---------------------------|----------------------------------|
| Cholesterol | | 20.7 | 362 |
| Triglyceride | C24:0 | 20.4 | 476 |
| | C30:0 | 20.0 | 572 |
| | C36:0 | 19.4 | 669 |
| | C42:0 | 18.9 | 765 |
| | C48:0 | 18.6 | 862 |
| | C54:0 | 17.9 | 959 |
| | C54:3 | 18.5 | 943 |
| | C54:6 | 19.1 | 927 |

Adapted from Arul, J., Boudreau, A., Makhlof, J., Tardif, R., and Gressier, B., *J. Dairy Res.*, 55, 361, 1988.

interest in a series of liquids may be studied, the polymer being assigned the δ value of the liquid providing the greatest solubility or the maximum swelling coefficient. This method may also be applied to high-molecular-weight mineral oils, dyes and similar compounds, from maxima in solubilities determined in liquids with various Hildebrand parameters. Thus, for the study of the distribution of cholesterol between the liquid fractions of milk fat,⁸⁷ Hildebrand parameters were determined by solvent spectrum and molar volumes by group contribution (Table 2). Other physical properties that can be studied include viscosity and related characteristic quantities such as grease dropping point (Section 14.7). In the case of solids (Section 12.1), the solute mole fraction solubility can be plotted against the solvent Hildebrand parameter to provide the solute δ value at the peak of the curve.

4.6 WILSON EQUATION

Both the Hildebrand-Scatchard model for molecules of similar size and the Flory-Huggins model for very dissimilar molecules (Section 13.2) assume zero enthalpy of mixing: athermal solutions.

Wilson^{9,46,84} consider the situation where components differ in intermolecular forces as well as molecular size; that is, where there are non-zero enthalpies of mixing. It was assumed that the Gibbs free energy change on mixing was given by a relation similar to the athermal Flory-Huggins equation, expressed in terms of "local" volume fractions ξ , and that probabilities of molecules occurring in each others' vicinities were given by Boltzmann factors, including interaction energies (${}^i u_g - {}^j u_g$) and (${}^i u_g - {}^j u_g$).

For polymers, a similar equation using local volume fractions and interaction energy differences has been developed by Heil and Prausnitz^{85,86} (Section 13.8).

REFERENCES

1. Hildebrand, J. H. and Carter, J. M., A study of van der Waals forces between tetrahalide molecules, *J. Am. Chem. Soc.*, 54, 3592, 1932.
2. Scatchard, G., Wood, S. E., and Mochel, J. M., Vapor-liquid equilibrium, V. Carbon tetrachloride-benzene mixtures, *J. Am. Chem. Soc.*, 62, 712, 1940.
3. Staveley, L. A. K., Tupman, W. I., and Hart, K. R., Some thermodynamic properties of the systems benzene + ethylene chloride, benzene + carbon tetrachloride, acetone + chloroform and acetone + carbon disulfide, *Trans. Faraday Soc.*, 51, 323, 1955.

4. Reed, T. M., III, The theoretical energies of mixing for fluorocarbon-hydrocarbon mixtures, *J. Phys. Chem.*, 59, 425, 1955; The polarizabilities of molecules in liquid mixtures, *J. Phys. Chem.*, 63, 1798, 1959.
5. Sonnich Thomsen, E., *The Energy of Mixing of Non-Polar Liquids. Reflections upon the Hildebrand Theory*, Thesis, Royal Danish School of Pharmacy, Copenhagen, 1965.
6. Sonnich Thomsen, E., The energy of mixing of non-polar liquids. Reflections upon the theories of Prigogine and Hildebrand, *Dansk Kemi*, 47(3), 35, 1966.
7. Sonnich Thomsen, E., Solubility Parameters, *Farmaceuten*, 29(3), 44, 1966; Present state of the solubility parameter theory, *Mitt. Chem. Gesell. DDR*, 16, 150, 1969.
8. Sonich Thomsen, E., Interaction between unlike nonpolar molecules: correction of the geometric mean rule. 1. Basic derivations. 2. Dilute systems. 3. Energies of mixing, *Acta Chem. Scand.*, 25, 260, 1971; 25, 265, 1971; 26, 2100, 1972.
9. Acree, W. E., Jr., *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, Orlando, FL, 1984.
10. van der Waals, J. D., *Z. Phys. Chem.*, 5, 133, 1890.
11. van Laar, J. J., *Sechs Vortrage uber das Thermodynamische Potential*, F. Vieweg, Braunschweig, 1906.
12. van Laar, J. J., The vapor pressure of binary mixtures, *Z. Phys. Chem.*, 72, 723, 1910; Theory of vapor pressure of binary mixtures, *Z. Phys. Chem.*, 83, 599, 1913; Relation between the deviation of the vapor pressure of binary mixtures of normal compounds from the straight line, and the heat of mixing, *Z. Phys. Chem.*, A, 137, 421, 1928.
13. Scatchard, G., Equilibria in non-electrolyte solutions in relation to the vapor pressures and densities of the components, *Chem. Rev.*, 8, 321, 1931.
14. Scatchard, G., Equilibrium in nonelectrolyte mixtures, *Chem. Rev.*, 44, 7, 1949.
15. Hildebrand, J. H., Solubility, *J. Am. Chem. Soc.*, 38, 1452, 1916.
16. Hildebrand, J. H., Solubility. III. Relative values of internal pressures and their practical application, *J. Am. Chem. Soc.*, 41, 1067, 1919.
17. Hildebrand, J. H., Compressibilities and thermal pressure coefficients of certain liquids, *Phys. Rev.*, 34, 649, 1929.
18. Hildebrand, J. H., Solubility. XII. Regular solutions, *J. Am. Chem. Soc.*, 51, 66, 1929.
19. Hildebrand, J. H., *Solubility of Non-Electrolytes*, 2nd ed., Reinhold, New York, 1936; Russian translation, GONTI, Moscow-Leningrad, 1938.
20. Hildebrand, J. H., A critique of the theory of solubility of non-electrolytes, *Chem. Rev.*, 44, 37, 1949.
21. Hildebrand, J. H., The term 'regular solution', *Nature (London)*, 168, 868, 1951.
22. Hildebrand, J. H., A simple correlation of gas solubilities, *J. Phys. Chem.*, 58, 671, 1954.
23. Hildebrand, J. H., Order from chaos, *Science*, 150, 441, 1965.
24. Hildebrand, J. H., Operation on swollen theories with Occam's razor, in *Structure-Solubility Relationships in Polymers* (Proc. Symp., 1976), Harris, F. W. and Seymour, R. W., Eds., Academic Press, New York, 1977, 1.
25. Hildebrand, J. H., Absence of outer non-bonding electrons in methyl groups affects solubility parameters, *Ind. Eng. Chem. Fundam.*, 17, 365, 1978.
26. Hildebrand, J. H., An improvement in the theory of regular solutions, *Proc. Natl. Acad. Sci. U.S.A.*, 76, 6040, 1979.
27. Hildebrand, J. H. and Dymond, J. H., Effect of methyl groups upon the solvent power of aliphatic liquids, *Proc. Natl. Acad. Sci. U.S.A.*, 54, 1001, 1965.
28. Hildebrand, J. H. and Lamoreaux, R. H., Solubility of gases in liquids; fact and theory, *Ind. Eng. Chem. Fundam.*, 13, 110, 1974.
29. Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L., *Regular and Related Solutions*, van Nostrand-Reinhold, Princeton, NJ, 1970.
30. Hildebrand, J. H. and Scott, R. L., *Solubility of Non-Electrolytes*, 3rd ed., Reinhold, New York, 1950; Dover, New York, 1964.
31. Hildebrand, J. H. and Scott, R. L., *Regular Solutions*, Prentice-Hall, Englewood Cliffs, NJ, 1962.
32. Scott, R. L., *Thesis*, Princeton, 1945.
33. Scott, R. L., The solubility of fluorocarbons, *J. Am. Chem. Soc.*, 70, 4090, 1948.
34. Scott, R. L., Theoretical models and real solutions, *Disc. Faraday Soc.*, 15, 44, 1953.
35. Staverman, A. J., Cohesion forces and phase theory of binary liquid systems, *Rec. Trav. Chim. Pays-Bas*, 60, 827, 1941.
36. Edelman, E., The cohesion factor concept and the solubility of macromolecular substances, *FATIPEC (Fed. Assoc. Tech. Ind. Peint. Vernis, Emaux Encres Impr. Eur. Cont.) Congr.*, 7, 160, 1964.
37. Harris, H. G. and Prausnitz, J. M., Thermodynamics of solutions with physical and chemical interactions, *Ind. Eng. Chem. Fundam.*, 8, 180, 1969.
38. Mandik, L., Dissolving capacity of hydrocarbon solvents for film forming substances. Critical solution point and solubility parameter, *Chem. Prum.*, 16, 545, 1966.

39. Kirchnerova, J. and Cave, G. C. B., The solubility of water in low-dielectric systems. *Can. J. Chem.*, 54, 3909, 1976.
40. Black, C., Joris, G. G., and Taylor, H. S., The solubility of water in hydrocarbons, *J. Chem. Phys.*, 16, 537, 1948.
41. Battino, R., Volume changes on mixing for binary mixtures of liquids, *Chem. Rev.*, 71, 5, 1971.
42. Bagley, E. B. and Scigliano, J. M., Polymer solutions, in *Solutions and Solubilities*, Part II, Dack, M. R. J., Ed., John Wiley & Sons-Interscience, New York, 1976, Chap. 16.
43. Ashton, N. F., McDermott, C., and Brench, A., Chemistry of extraction of nonreacting solutes, in *Handbook of Solvent Extraction*, Lo., T. C., Baird, M. H. I., and Hanson, C., Eds., John Wiley & Sons-Interscience, New York, 1983, chap. 1, 3.
44. Kaelble, D. H., *Physical Chemistry of Adhesion*, John Wiley & Sons-Interscience, New York, 1971.
45. Lee, L. L., A molecular theory of solubility parameters: generalization to polar fluid mixtures, *Fluid Phase Equil.*, 35, 77, 1987.
46. Prausnitz, J. M., *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ, 1969.
47. Prausnitz, J. M., Lichtenthaler, R. N., and Gomez de Azevedo, E., *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1986.
48. Brandts-Buys, L. and Huyskens, P., Limitations of the concept of 'solubility parameter', *FATIPEC (Fed. Assoc. Tech. Ind. Peint. Vernis, Emaux Encres Impr. Eur. Cont.) Congr.*, 16 (Liege), 191, 1982.
49. Hansen, C. M., Characterization of surfaces by spreading liquids, *J. Paint Technol.*, 42, 660, 1970.
50. Drahos, J., Liquid-vapor equilibrium. LXXVII. Comparison of the volume and surface modifications of the regular solution model, *Collect. Czech. Chem. Commun.*, 43, 805, 1978.
51. Drahos, J., Wichterle, I., and Hala, E., A generalized method for calculation and prediction of vapor-liquid equilibria at high pressures, *Fluid Phase Equil.*, 1, 1973, 1977/78.
52. Erdős, E., Liquid-vapor equilibria. XV. Calculation of the constants in the van Laar equation from the properties of the pure components, *Collect. Czech. Chem. Commun.*, 21, 1528, 1956.
53. Sazonov, V. P. and Gudkina, L. V., Liquid-phase equilibria between the components of the ternary system diamyl ether-acetonitrile-glycerol, *Zh. Prik. Khim.*, 47, 2515, 1974; *J. Appl. Chem. U.S.S.R.*, 47, 2587, 1974.
54. Stallard, R. D. and Amis, E. S., Heat of vaporization and other properties of dioxane, water and their mixtures, *J. Am. Chem. Soc.*, 74, 1781, 1952.
55. Iscan, M., The solubility of aniline in the mixture of *n*-hexane + cyclohexane, *Istanbul Univ. Fen. Fak. Mecm. Ser.C.*, 39, 195, 1974—1976 (pub. 1977).
56. Lui, P. C. K. and Donnelly, H. G., Determination of liquid-mixture solubility parameters and interaction energy densities, *Am. Inst. Chem. Eng. J.*, 19, 574, 1973.
57. Martin, A., Paruta, A. N., and Adjei, A., Extended Hildebrand solubility approach: methylxanthines in mixed solvents, *J. Pharm. Sci.*, 70, 1115, 1981.
58. Martin, A. and Miralles, M. J., Extended Hildebrand solubility approach: solubility of tolbutamide, acetohexamide, and sulfisomidine in binary solvent mixtures, *J. Pharm. Sci.*, 71, 439, 1982.
59. Martin, A., Wu, P. L., Adjei, A., Lindstrom, R. E., and Elworthy, P. H., Extended Hildebrand solubility approach and the log linear solubility equation, *J. Pharm. Sci.*, 71, 849, 1982.
60. Martin, A., Wu, P. L., Adjei, A., Mehdzadeh, M., James, K. C., and Metzler, C., Extended Hildebrand solubility approach: testosterone and testosterone propionate in binary solvents, *J. Pharm. Sci.*, 71, 1334, 1982.
61. Wu, P. L. and Martin, A., Extended Hildebrand solubility approach: *p*-hydroxybenzoic acid in mixtures of dioxane and water, *J. Pharm. Sci.*, 71, 849, 1982.
62. Mandik, L., Additivity of the critical solution temperatures of hydrocarbons with aniline, *Collect. Czech. Chem. Commun.*, 31, 3869, 1966.
63. Purkayastha, A. and Walkley, J., Studies in solubility parameter theory for mixed solvent systems, *Can. J. Chem.*, 50, 834, 1972.
64. Burrell, H., Solubility parameters, *Interchem. Rev.*, 14, 3—16 and 31—46, 1955.
65. Wolf, B. A. and Willms, M. M., Measured and calculated solubility of polymers in mixed solvents: cononsolvency, *Makromol. Chem.*, 179, 2265, 1978.
66. Hamaker, H. C., The London-van der Waals attraction between spherical particles, *Physica (Utrecht)*, 4, 1058, 1937.
67. Visser, J., Colloid and other forces in particle adhesion and particle renewal (a review), in *Deposition and Filtration of Particles from Gases and Liquids*, Society of Chemical Industry, London, 1978.
68. Purkayastha, A., *Studies in Regular Solution Theory*, Thesis, Simon Fraser University, British Columbia, 1971; *Diss. Abstr. Int. B*, 32, 1406, 1971.
69. Christian, S. D., Solvent effects on molecular complex formation. Pyridine-iodine system, *J. Am. Chem. Soc.*, 91, 6514, 1969.

70. Nakanishi, K. and Asakura, S., Solubility of iodine in mixed solvents. A case study of preferential solvation in non-polar and associated solutions, *J. Phys. Chem.*, 81, 1745, 1977.
71. Froehling, P. E., Koenhen, D. M., Bantjes, A., and Smolders, C. A., Swelling of linear polymers in mixed swelling agents; predictability by means of solubility parameters, *Polymer*, 17, 835, 1976.
72. Rigbi, Z., Prediction of swelling of polymers in 2 and 3 component mixtures, *Polymer*, 19, 1229, 1978.
73. Froehling, P. E. and Hillegers, L. T., Solubility parameters of ternary solvent mixtures. Calculation of the solvent composition with maximum polymer interaction, *Polymer*, 22, 261, 1981.
74. Behnken, D. W., Calculation of optimum multicomponent solvent compositions for polymers using a multiple regression program, *Polymer*, 24, 193, 1983.
75. Mizerovskii, L. N. and Belova, O. V., Calculation of the solubility parameter of binary mixtures of liquids and copolymers, *Vysokomol. Soedin. Ser. A.*, 29, 1236, 1987; *Polym. Sci. U.S.S.R.*, 29, 1987.
76. Burrell, H., Solubility parameters for film formers, *Off. Dig. Fed. Paint Varn. Prod. Clubs*, 27, 726, 1955.
77. Lazurin, E. A., Samorodov, V. T., and Kosmodemyanskii, L. V., Determination of solubility parameters of mineral oils, *Promst. Sint. Kauch.* No. 8, 10, 1980; *Int. Polym. Sci. Tech.*, 8(12), T12, 1981.
78. Piskarev, V. A. and Radushkevich, R. L., Method for determining the compatibility of bitumens with elastomers, *Polim. Stroit. Mater.*, 42, 163, 1975.
79. Vasitakos, N. P. and Lawson, D. D., Solubility parameter spectroscopy in coal extraction, *Liq. Fuels Technol.*, 3, 305, 1985.
80. Siddiqui, S. A., Studies of solvent dyeing. Part I: Preparation of disperse dyes and determination of their solubility parameters, *Text. Res. J.*, 51, 527, 1981.
81. Siddiqui, S. A. and Needles, H. L., Solubility parameters, *Text. Res. J.*, 52, 570, 1982.
82. Siddiqui, S. A., Determining the solubility parameter of dyes; Dye solubility by solubility method, *Am. Dyest. Rep.*, 72(3), 30, 1983; 2(4), 36, 1983.
83. Burrell, H., Solubility parameter values, in *Polymer Handbook*, Brandrup, J. and Immergut, E. H., Eds., John Wiley & Sons-Interscience, New York, 1966, IV—341; 2nd ed., 1975, IV—337.
84. Wilson, G. M., Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing, *J. Am. Chem. Soc.*, 86, 127, 1964.
85. Heil, J. F., *Phase Equilibria in Multi-Component Polymer Solutions*, Doctoral Dissertation, University of California, Berkeley, 1965; *Diss. Abstr.*, 26, 7196, 1966.
86. Heil, J. F. and Prausnitz, J. M., Phase equilibria in polymer solutions, *Am. Inst. Chem. Eng. J.*, 12, 678, 1966.
87. Arul, J., Boudreau, A., Makhlof, J., Tardif, R., and Gressier, B., Distribution of cholesterol in milk fat fractions, *J. Dairy Res.*, 55, 361, 1988.
88. Tucker, S. A., Murrall, D. J., Oswald, B. M., Halmic, J. L., and Acree, W. E., Jr., Solubility of anthracene in binary toluene and alkane solvent mixtures, *Phys. Chem. Liq.*, 18, 279, 1988.
89. Bissell, M., Chittick, C. E., and Acree, W. E., Jr., Solubility of anthracene in binary solvent mixtures containing tetrahydrofuran, *Fluid Phase Equil.*, 41, 187, 1988.
90. McCargar, J. W. and Acree, W. E., Jr., Thermochemical investigations of associated solutions, VI. Mole fraction versus volume fraction based equilibrium constants; Solubility of carbazole in binary chloroalkane and dibutyl ether solvent mixtures, *J. Solution Chem.*, 17, 1081, 1988 and 18, 151, 1989.
91. Wallach, J. R., Tucker, S. A., Oswald, B. M., Murrall, D. J., and Acree, W. E., Jr., Solubility of pyrene in binary solvent mixtures containing dibutyl ether, *J. Chem. Eng. Data*, 34, 70, 1989.
92. Durbut, P. and Broze, G., Application of the solubility parameter theory to fatty soil removal, *Commun. Journ. Cons. Esp. Deterg.*, 20, 383, 1989.

Chapter 5

EXPANDED COHESION PARAMETERS

So far in this development of the cohesion parameter approach to miscibility and other interaction properties, the existence of polar interactions and of specific effects such as hydrogen bonding has been neglected while the traditional Hildebrand description of regular or near-regular systems was explored.

Accommodation of interactions which do not conform to geometric mean behavior (Section 4.1) has been approached in two main ways. On the one hand empirical corrections have been made for geometric mean deviations (Section 5.7), and on the other the Hildebrand parameter has been subdivided into various component cohesion parameters. The most general formalism was introduced by Karger, Keller, Snyder, and Eon,¹⁻⁸ who developed it for the optimization of chromatographic selectivity, although it has proved too cumbersome for widespread use so far. The most widely used method has been a three-component parameter proposed by Hansen⁹⁻³⁰ for the empirical description of polymer-liquid systems (Section 5.9). There have been several other variations developed for practical applications, the one with most promise being perhaps that of Beerbower, Martin, and Wu,^{31,32} (Section 5.12) which provides an acceptable compromise between rigor and simplicity.

To be generally useful, theories or models attempting to systematize the behavior of matter must deal with molecular interactions by providing information about their origins and natures as well as about their strengths. The cohesive properties characteristic of the condensed states of matter are produced by the various intermolecular forces described in Chapter 3. The cohesive pressures ${}^i c$, ${}^j c$, and ${}^i j c$ represent the resultant effect of these forces acting between molecules of types i and j , and from Equation 10, Chapter 4, the cohesive pressure of the mixture relative to the components is

$${}^i j A = {}^i c + {}^j c - 2{}^i j c$$

where

$${}^i c = {}^i \delta^2 \text{ and } {}^j c = {}^j \delta^2$$

5.1 DISPERSION

Dispersion or London forces, which can be considered as arising from the fluctuating dipoles which result from a positive nucleus and a negative electron "cloud" in each atom, occur in all molecules, whether polar or not. The dispersion cohesive pressure of a pure material i is here denoted ${}^i c_d$, and the corresponding cohesion parameter, δ_d , is defined by

$$- {}^i U_d / V = {}^i c_d = {}^i \delta_d^2 \quad (1)$$

It can be shown on the basis of London theory that the nonpolar, dispersive interactions between unlike molecules of types i and j provide a contribution to the cohesive pressure which is approximated by the geometric mean of the individual values and is given by

$${}^i j c_d = ({}^i c_d {}^j c_d)^{1/2} = {}^i \delta_d {}^j \delta_d \quad (2)$$

A simple interpretation of this "geometric mean" behavior is that the interaction is of a "symmetrical" nature: each member of a pair of molecules interacts by virtue of the same property, the polarizability. (The ionization potentials, which also appear in Equation 6, Chapter 3, have similar values for most organic compounds, i.e., ${}^i I \approx {}^j I$.) It follows that

$${}^iA_d = {}^i\delta_d^2 + {}^j\delta_d^2 - 2 {}^i\delta_d {}^j\delta_d = ({}^i\delta_d - {}^j\delta_d)^2 \quad (3)$$

For nonpolar molecules, dispersion forces should make the only contributions to the cohesive pressure, so from Equation 5, Chapter 2,

$${}^i\delta_d = (\Delta U / {}^iV)^{1/2} \quad (4)$$

However, it is of interest that hydrocarbons possessing methyl groups show iodine solution behaviors consistent with Hildebrand parameter values significantly greater than those given by Equation 4, even though the solutions are violet in color and therefore "non-associated" (unlike the straw-colored aqueous solutions, for example). In fact, the extent of deviation from Equation 4, $[\delta - (\Delta U / {}^iV)^{1/2}]$, is proportional to the number of methyl groups in these molecules,^{33,34} a fact attributed to a variation in the extent of the dispersion forces in molecules with a high proportion of saturated C-H bonding.

The dispersion cohesion parameter can be calculated by the homomorph method (Sections 6.7 and 6.8) or from the refractive index (Section 8.2). Beerbower and Jensen³⁵ have reviewed the correlation between dispersion properties and the "softness" in the Pearson "hard or soft" acid-base concept (Section 5.12).

5.2 ORIENTATION

Orientation effects that result from dipole-dipole or Keesom interactions occur between molecules which have permanent dipole moments. The orientation cohesive pressure of a pure material *i* is denoted ${}^i c_o$, and the corresponding orientation cohesion parameter, ${}^i\delta_o$, is defined by

$$- {}^iU_o / {}^iV = {}^i c_o = {}^i\delta_o^2 \quad (5)$$

Like dispersion forces, these are "symmetrical" interactions depending on the same property of each molecule, which in this case is the dipole moment as shown in Equation 4, Chapter 3. It follows that the geometric mean approximation is well obeyed for orientation interactions even between unlike molecules.³⁶ For polar molecules that may be represented by spherical force fields with small ideal dipoles at their centers, this contribution to the cohesive pressure in mixtures of *i* and *j* molecules is

$${}^i c_o = ({}^i c_o {}^j c_o)^{1/2} = {}^i\delta_o {}^j\delta_o \quad (6)$$

The interchange cohesive pressure due to orientation is

$${}^iA_o = ({}^i\delta_o - {}^j\delta_o)^2 \quad (7)$$

Keller, Karger, and Snyder⁵ and Munafo, Buchmann, Hô Nam-Tran and Kesselring³⁷ are among those to have discussed the evaluation of orientation and induction components from dipole moments and relative permittivities: see also Section 8.2.

5.3 INDUCTION

Dipole induction effects arise from dipole-induced dipole or Debye interactions occurring between molecules with permanent dipole moments and any other neighboring molecules, whether polar or not, and result in an induced nonuniform charge distribution. In contrast to dispersion and orientation interactions, dipole induction interactions are "unsymmetrical", involving the dipole moment of one molecule and the polarizability of the other (Chapter

3). Consequently, the cohesive pressure term for induction in a pure material i involves the product $\delta_i \delta_d$, where δ_i is the induction cohesion parameter. Similarly, in a mixture of i and j

$$y_{c_i} = \delta_i \delta_d + \delta_j \delta_d \quad (8)$$

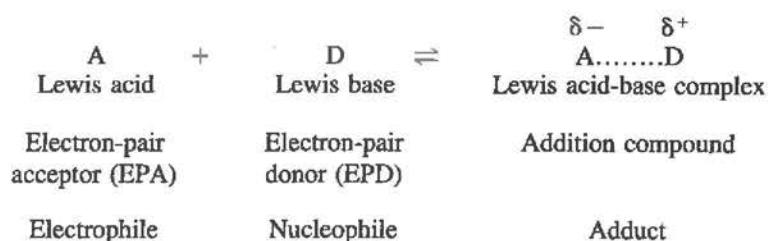
Therefore it can be shown that

$$y_{A_i} = 2 \delta_i \delta_d + 2 \delta_j \delta_d - 2 \delta_i \delta_d - 2 \delta_j \delta_d \quad (9)$$

$$= 2(\delta_d - \delta_i)(\delta_i - \delta_j) \quad (10)$$

5.4 LEWIS ACID-BASE

Lewis acid-base or electron donor-acceptor interactions, which have been reviewed frequently,* can be denoted by the equation



The Lewis acid-base complex is formed by an overlap between a filled electron orbital of sufficiently high energy in the donor molecule and a vacant orbital of sufficiently low energy (high electron affinity) in the acceptor molecule. This type of interaction differs from a "normal" chemical bond in that only one type of molecule (the donor) supplies the pair of electrons, rather than each type of molecule supplying one electron. More than one electron must be involved, and coordination of the Lewis acid to the Lewis base must occur. Electron-pair donors are of three types:

1. n -EPD molecules, where the electrons donated are the lone pair of n (nonbonding) electrons of hetero atoms in compounds such as R_2O , R_3N , R_2SO , where R is an alkyl group
2. σ -EPD molecules, which donate the electron-pair of a σ -bond, as in alkyl halides and cyclopropane
3. π -EPD molecules, using the pair of π -electrons of unsaturated and aromatic compounds such as alkenes, alkylbenzenes and polycyclic aromatics

Electron-pair acceptor molecules also may be divided into three groups:

1. ν -EPA, in which the lowest orbital is a vacant (ν) valence orbital of a metal atom, such as Ag^+ and some organometallics
2. σ -EPA, which use a nonbonding σ orbital, as in halogens or interhalogens
3. π -EPA, in the case of molecules with a π -bond system (aromatic and unsaturated compounds) with electron-withdrawing substituents, for example, aromatic polynitro compounds, halogenated benzoquinones, and tetracyanoethylene

* For example: Arnett;³⁸ Bent;^{39,40} Coetzee and Ritchie;⁴¹ Drag, Lim, and Matwiyoff;^{42,43,47} Jensen;⁴⁴⁻⁴⁶ Reichardt;⁴⁸ and Wrona.⁴⁹

All nine types of EPD-EPA complexes resulting from combinations of these donors and acceptors exist, with bond strengths ranging from high values (*n*-EPD/*v*-EPA) to very weak interactions (π -EPD/ π -EPA effects between neutral molecules). Ion solvation (Section 12.3) also may be treated in terms of Lewis acid-Lewis base interactions.

Many authors have pointed out that electron donating and accepting properties can be discussed in terms of acid-base cohesion parameters.^{1-6,50-55} Lewis acid-base interactions are "unsymmetrical", involving a donor and an acceptor with different roles (rather than two equivalent participants as in dispersion interactions, which are "symmetrical"). It is apparent, therefore, that it is necessary to use two separate cohesion parameters for each partner to characterize these interactions, and this may be done in terms of a Lewis acid cohesion parameter (δ_a) and a Lewis base cohesion parameter (δ_b), in a manner analogous to that for induction interactions:

$${}^iA_{ab} = 2 ({}^i\delta_a - {}^j\delta_a)({}^i\delta_b - {}^j\delta_b) \quad (12)$$

Clearly from this equation the maximum interaction (${}^iA_{ab}$ large and negative) occurs when

$${}^i\delta_a = {}^j\delta_b = 0, {}^iA_{ab} = -2 {}^i\delta_a {}^j\delta_b \quad (13)$$

and when

$${}^j\delta_a = {}^i\delta_b = 0, {}^iA_{ab} = -2 {}^j\delta_a {}^i\delta_b \quad (14)$$

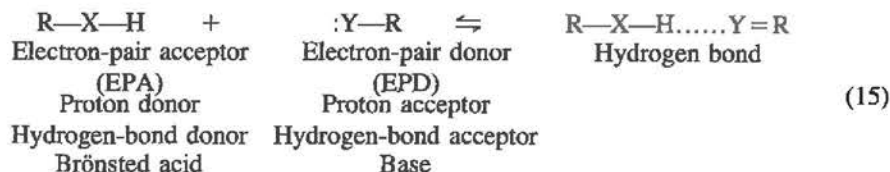
When ${}^iA_{ab}$ is large and negative, exothermic mixing is possible, in contrast to mixing being restricted to athermic or endothermic processes, which is the case when only dispersion and polar forces exist. These acid-base cohesion parameters have something in common with the four-parameter acid-base equation of Drago (Section 7.12).

In those situations where donor-acceptor complexes are formed to such an extent that there is an appreciable proportion of identifiable new compound in the mixture, it may be necessary to evaluate the cohesion parameters of this new species so that it can be used in the estimation of thermodynamic properties such as activity coefficients. Approaches to this problem have included using the arithmetic mean of the donor and acceptor parameters⁵⁶ and volume-weighted averages (Equation 31, Chapter 4).⁵⁷ The topic is considered further in Section 7.9.

Acid-base interactions are not restricted to solutions, but occur in all types of systems, including pigment dispersions^{54,55} (as illustrated in later chapters).

5.5 HYDROGEN BONDING ASSOCIATION

Hydrogen-bonding interaction is a particular type of Lewis acid-base reaction in which the electron acceptor is a Brönsted acid. A convenient definition is that a hydrogen bond is a second bond formed to another atom by a covalently bound hydrogen atom. In the following scheme, atoms X and Y have electronegativities (relative tendencies of the bonded atom to attract electrons) higher than that of H, for example, C, N, P, O, S, F, Cl, Br, or I:



The classification by Pimentel and McClellan⁵⁸ of liquids according to their hydrogen-bonding characteristics has been used widely.^{53,59}

- *Proton donor*, such as trichloromethane
- *Proton acceptor*, such as ketones, aldehydes, esters, ethers, tertiary amines, aromatic hydrocarbons, alkenes
- *Proton donor/acceptor*, such as alcohols, carboxylic acids, water, primary and secondary amines
- *Proton non-donor/non-acceptor* such as alkanes, carbon disulfide, tetrachloromethane

On this basis, it is possible to predict immediately in a qualitative way the extent of contribution that hydrogen bonding is likely to make to the interchange cohesive pressure, ${}^iA_{ab}$. Any net increase in the extent of hydrogen bonding as a result of mixing decreases ${}^iA_{ab}$ and so favors miscibility. Thus, miscibility is enhanced if hydrogen bonds are formed when two liquids without hydrogen bonding (such as trichloromethane and acetone) are mixed, while it is reduced if hydrogen bonding in the component liquids is destroyed (as in water being mixed with an alkane).

It is apparent that two pairs of parameters to characterize these interactions are necessary, and this may be done using the Lewis acid-base formalism, Equation 12.

$${}^iA_{ab} = 2 ({}^i\delta_a - {}^j\delta_a)({}^i\delta_b - {}^j\delta_b) \quad (17)$$

In this situation the parameters δ_a and δ_b are then equivalent to the parameters σ and τ proposed by Small.⁶⁰ Rider^{61,62} developed an alternative two-parameter donor-acceptor model for predicting polymer-liquid interactions (Section 7.12); the parameters in this model are determined from experimental information including frequency shifts, solubilities, and acid-base properties.

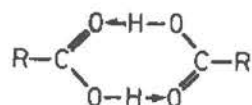
Variations in properties resulting from hydrogen-bonding interactions can be looked at from other points of view. Chastrette and co-workers⁶³ have observed from multivariate statistical analysis of solubility information that a liquid may have more than one point in hyperspace associated with it: for different chemical applications one point is more relevant than the other.

Another approach to hydrogen bonding is to consider it as a chemical reaction (as suggested in the previous section), producing new molecules which then interact with the other components. Renon and Prausnitz,⁶⁴ Wiehe and Bagley,⁶⁵ and Bagley and Chen⁶⁶ have studied the relatively simple situation of an alcohol mixed with an alkane. This can be considered as a self-associated component (the alcohol) interacting with a nonassociated component (the alkane), and suggests a clear division into "chemical" (subscript C) and "physical" (subscript P) interactions. It is assumed that the alcohol exists in solution in the form of linear, hydrogen-bonded polymers which interact with each other by physical processes only. In terms of excess Gibbs free energies of mixing,

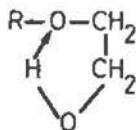
$${}^E\Delta_m G = {}^E\Delta_m G_C + {}^E\Delta_m G_P \quad (18)$$

where ${}^E\Delta_m G_P$ is given by an expression of the form of Equation 35, Chapter 4, and ${}^E\Delta_m G_C$ is an expression involving an equilibrium constant describing the hydrogen bonding. A similar procedure was used for acetylene in various hydrogen-bonding liquids.⁶⁷ Kirchnerova and Cavé⁶⁸ assumed water-organic complexes when discussing the solubility of water in low permittivity liquids in terms of cohesion parameters, and defined $-U_h$ as the cohesive energy corresponding to the energy change associated with the notional process of real water being converted into a hypothetical liquid of dipolar monomers.

In situations where only hydrogen bond dimerization is significant, correction can be made in the cohesion parameter values in the simpler manner⁶⁹ illustrated in Equation 20, Chapter 6. Examples are carboxylic acids,

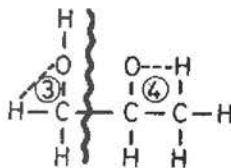


and glycol ethers such as Cellosolves® and Carbitols®



In such cases the result is that the dimer has a cohesion parameter significantly different from that of the monomer, and so is expected to have different solubility characteristics. This is in agreement with the observation that a material like acetic acid is soluble in such diverse liquids as water and heptane. Thus, in polar liquids these compounds are capable of interacting as if they are polar, while in nonpolar liquids the polar interactions are "self-contained" or "internal" and the dimeric molecules tend to behave in a nonpolar manner. Hoy⁶⁹ proposed that this ability to assume the character of the environment be termed *chameleonic*, after the reptile which is able to adopt the color of its background. The dimerization of several carboxylic acids has been assessed in terms of cohesion parameters.⁷⁰⁻⁷²

Huyskens, Haulait-Pirson, Siegel and Kapuku^{153,154,162} preferred to consider hydrogen bonds in liquids as the cohesive forces with the longest lifetime, and introduced the concept of "mobile disorder". Accommodation of such variations in cohesion properties by means of corrections to the geometric mean approximation is discussed in Section 5.7. Nisbet⁷⁵ took intramolecular hydrogen bonding into account by considering the formation of all possible pseudo ring structures in alcohol molecules, with interaction energies evaluated for dispersion, polar, and hydrogen-bonding components. Three- and four-membered rings are illustrated by:



Martin, Wu, Liron, and Cohen⁷³ proposed an approach to the chameleonic behavior problem in drug solutions which assumed a virtual solute cohesion parameter Λ made up of a constant, invariant Hildebrand parameter δ and a variable (chameleonic) term Γ which depends on the Walker solute-solvent interaction parameter θK (see Section 5.7):

$$\Lambda^2 = \delta^2 + \Gamma^2 \quad (19)$$

The variable cohesion parameter of a solute obtained from observations of interactions with relatively polar liquids would then be designated not δ but Λ , and the (invariant) Hildebrand parameter would be determined from vaporization enthalpy as proposed originally, or by interaction with relatively nonpolar liquids with which it formed near-regular solutions.

Kamlet, Doherty, Taft, and Abraham⁷⁴ incorporated cohesion parameters in their linear solvation energy approach to self-association in water and alcohols; further details appear in Chapter 8.

5.6 COMBINATION OF COMPONENT COHESION PARAMETERS

One of the assumptions central to the cohesion approach to interactions is that the various contributions to the cohesive pressure of a fluid (either pure or mixed) are additive, so the interchange cohesive pressure or exchange energy density for a system is:

$${}^i u_A = {}^i u_{A_d} + {}^i u_{A_o} + {}^i u_{A_i} + {}^i u_{A_{ab}} \quad (20)$$

$$= ({}^i \delta_d - {}^j \delta_d)^2 + ({}^i \delta_o - {}^j \delta_o)^2 + 2({}^i \delta_d - {}^j \delta_d)({}^i \delta_i - {}^j \delta_i) + 2({}^i \delta_a - {}^j \delta_a)({}^i \delta_b - {}^j \delta_b) \quad (21)$$

$$= {}^i \delta_i^2 + {}^j \delta_i^2 - 2 {}^i \delta_d {}^j \delta_d - 2 {}^i \delta_o {}^j \delta_o - 2 {}^i \delta_i {}^j \delta_d - 2 {}^j \delta_i {}^i \delta_d - 2 {}^i \delta_a {}^j \delta_b - 2 {}^j \delta_a {}^i \delta_b \quad (22)$$

where ${}^i \delta_i$ is the Hildebrand parameter or total cohesion parameter for component i (evaluated from vaporization energy — see Chapter 7) and related to the component parameters by

$${}^i \delta_i^2 = {}^i \delta_d^2 + {}^i \delta_o^2 + 2 {}^i \delta_i {}^i \delta_d + 2 {}^i \delta_a {}^i \delta_b \quad (23)$$

or, omitting the superscript i and subscript t for simplicity when there is no ambiguity possible:

$$\delta^2 = \delta_d^2 + \delta_o^2 + 2\delta_i \delta_d + 2\delta_a \delta_b \quad (24)$$

It is clear that two types of term appear in these equations, quadratic terms (symmetrical) for dispersion and orientation, and double product or cross terms (unsymmetrical) for induction and acid-base interactions. The geometric mean assumption (Equation 12, Chapter 4) is clearly inadequate for the total or Hildebrand parameters in the presence of these cross terms:

$${}^i u_c = ({}^i c {}^j c)^{1/2} = {}^i \delta {}^j \delta \quad (25)$$

The approach taken by Karger, Snyder, and Eon⁴ was to calculate the dispersion term from the refractive index, the induction and orientation terms from the dipole moment and molar volume (or δ_i from retention volumes in gas-liquid chromatography), and $2 \delta_a \delta_b$ by difference. The original estimates of these component cohesion parameters for a few common liquids are presented in Table 1. The origins of the various types of cohesion properties of different liquids with similar total cohesion parameters are here apparent, although the precise values of the individual parameters are open to question. A related set of parameters is introduced in Section 5.13.

If hydrogen-bonding capability is absent, it is reasonable to exclude the acid and base components; such an approach was taken by Melder and Ebber,⁷⁶⁻⁷⁹ allowing an emphasis on dispersion, orientation, and induction components. Ignat and Melder^{80,81} subsequently determined the components of the cohesion parameters of alcohols (Table 2), based on the experimental activity coefficients of alcohols in nonpolar liquids and the partial enthalpies of dissolution in water (for which component values also appear in Table 2). Later, they¹⁶¹

TABLE 1
Five-Component Cohesion Parameters of Liquids in Order of Increasing
Hildebrand Parameter¹⁻⁴

| Liquid | $\delta/\text{MPa}^{1/2}$ | | | | | | $V/\text{cm}^3\text{mol}^{-1}$ |
|--------------------------------|---------------------------|------------|------------|------------|------------|------------|--------------------------------|
| | δ_1 | δ_2 | δ_3 | δ_4 | δ_5 | δ_6 | |
| Perfluoroalkanes | ~12 | ~12 | — | — | 2.1 | — | — |
| Pentane | 14.5 | 14.5 | — | — | — | — | 115 |
| Diisopropyl ether | 14.5 | 14.1 | 2.1 | 0.2 | — | 6.1 | 102 |
| Hexane | 14.9 | 14.9 | — | — | — | — | 131 |
| Diethyl ether | 15.3 | 13.7 | 4.9 | 1.0 | — | 6.1 | 105 |
| Triethylamine | 15.3 | 15.3 | — | — | — | 9.2 | 140 |
| Cyclohexane | 16.8 | 16.8 | — | — | — | — | 108 |
| Chloropropane, 1-chloropropane | 17.2 | 14.9 | 5.9 | 1.2 | — | 1.4 | 88 |
| Tetrachloromethane | 17.6 | 17.6 | — | — | — | 1.0 | 97 |
| Diethyl sulfide | 17.6 | 16.8 | 3.5 | 0.5 | — | 5.3 | 108 |
| Ethyl acetate | 18.2 | 14.3 | 8.2 | 2.1 | — | 5.5 | 98 |
| Propylamine | 18.2 | 14.9 | 3.5 | 0.4 | 3.7 | 11.3 | 82 |
| Bromoethane | 18.2 | 16.0 | 6.3 | 1.2 | — | 1.6 | 77 |
| Toluene | 18.2 | 18.2 | — | — | — | 1.2 | 107 |
| Tetrahydrofuran | 18.6 | 15.5 | 7.2 | 1.6 | — | 7.6 | 82 |
| Benzene | 18.8 | 18.8 | — | — | — | 1.2 | 89 |
| Trichloromethane | 19.0 | 16.6 | 6.1 | 1.0 | 13.3 | 1.0 | 81 |
| Methyl Ethyl ketone | 19.4 | 14.5 | 9.6 | 2.5 | — | 6.5 | 90 |
| Acetone, 2-propanone | 19.6 | 13.9 | 10.4 | 3.1 | — | 6.1 | 74 |
| 1,2-Dichloroethane | 19.8 | 16.8 | 8.6 | 1.0 | — | 1.4 | 79 |
| Anisole, methoxybenzene | 19.8 | 18.6 | 4.3 | 0.8 | — | 3.5 | 109 |
| Chlorobenzene | 19.8 | 18.8 | 3.9 | 0.6 | — | 2.1 | 102 |
| Bromobenzene | 20.2 | 19.6 | 3.1 | 0.4 | — | 2.1 | 105 |
| Iodomethane | 20.2 | 19.0 | 5.1 | 0.6 | — | 1.4 | 62 |
| 1,4-Dioxane | 20.7 | 16.0 | 10.6 | 2.1 | — | 9.4 | 86 |
| Hexamethylphosphoramide | 21.5 | 17.2 | 7.0 | 3.5 | — | 8.2 | 176 |
| Pyridine | 21.7 | 18.4 | 7.8 | 2.1 | — | 10.0 | 81 |
| Acetophenone | 21.7 | 19.6 | 5.5 | 1.4 | — | 6.8 | 117 |
| Benzonitrile | 21.9 | 18.8 | 7.0 | 2.1 | — | 4.7 | 103 |
| Propionitrile | 22.1 | 14.1 | 13.5 | 3.7 | — | 4.3 | 71 |
| Quinoline | 22.1 | 21.1 | 3.7 | 0.6 | — | 8.6 | 118 |
| <i>N,N</i> -Dimethylacetamide | 22.1 | 16.8 | 9.6 | 3.3 | — | 9.2 | 92 |
| Nitroethane | 22.5 | 14.9 | 12.3 | 4.5 | — | 2.1 | 71 |
| Nitrobenzene | 22.7 | 19.4 | 7.4 | 2.3 | — | 2.1 | 103 |
| Tricresyl phosphate | 23.1 | 19.6 | 5.1 | 3.1 | — | (?) | 316 |
| <i>N,N</i> -Dimethylformamide | 24.1 | 16.2 | 12.7 | 4.9 | — | 9.4 | 77 |
| 1-Propanol | 24.5 | 14.7 | 5.3 | 0.8 | 12.9 | 12.9 | 75 |
| Dimethylsulfoxide | 24.5 | 17.2 | 12.5 | 4.3 | — | 10.6 | 71 |
| Acetonitrile | 24.7 | 13.3 | 16.8 | 5.7 | — | 7.8 | 53 |
| Phenol | 24.7 | 19.4 | 4.7 | 0.8 | 19.0 | 4.7 | 92 |
| Ethanol | 26.0 | 13.9 | 7.0 | 1.0 | 14.1 | 14.1 | 59 |
| Nitromethane | 26.4 | 14.9 | 17.0 | 6.1 | — | 2.5 | 54 |
| γ -Butyrolactone | 26.4 | 16.4 | 14.7 | 6.5 | — | (?) | 77 |
| Propylene carbonate | 27.2 | 20.0 | 12.1 | 4.9 | — | (?) | 85 |
| Diethylene glycol | 29.2 | 16.8 | 8.2 | 1.2 | 10.8 | 10.8 | 96 |
| Methanol | 29.7 | 12.7 | 10.0 | 1.6 | 17.0 | 17.0 | 41 |
| Ethylene glycol | 34.8 | 16.4 | 13.9 | 2.3 | 12.5 | 12.5 | 56 |
| Formamide | 39.3 | 17.0 | (?) | (?) | (large) | (large) | 40 |
| Water | 47.9 | 12.9 | (?) | (?) | (large) | (large) | 18 |

TABLE 2
Five-Component Cohesion Parameters for Alcohols

| Liquid | $\delta/\text{MPa}^{1/2}$ | | | | | |
|---------------------------------|---------------------------|------------|------------|------------|------------|------------|
| | δ_a | δ_b | δ_c | δ_d | δ_e | δ_f |
| 1-Propanol | 14.9 | 6.7 | 4.5 | 4.8 | 23.5 | 25.0 |
| Isobutanol, 2-methyl-1-propanol | 15.0 | 5.8 | 3.4 | 3.8 | 22.8 | 23.1 |
| 1-Butanol | 15.3 | 5.4 | 3.1 | 4.6 | 22.6 | 23.8 |
| 2-Butanol, <i>sec</i> -butanol | 15.2 | 5.4 | 3.2 | 3.5 | 23.3 | 22.8 |
| 1-Pentanol, amyl alcohol | 15.7 | 4.7 | 2.9 | 3.7 | 21.9 | 22.8 |
| 1-Hexanol | 15.9 | 3.7 | 1.7 | 4.0 | 21.5 | 22.1 |
| Cyclohexanol | 17.3 | 5.4 | 2.9 | 2.1 | 21.2 | 22.7 |
| 1-Octanol | 16.2 | 3.1 | 1.8 | 3.6 | 17.8 | 21.1 |
| 1-Nonanol | 16.3 | 2.8 | 1.7 | 3.4 | 17.2 | 20.7 |
| 1-Decanol | 16.4 | 2.0 | 0.9 | 3.8 | 16.8 | 20.5 |
| Anisole | 18.5 | 3.5 | 1.4 | 0.0 | 16.5 | 30.2 |
| Butyl acetate | 15.0 | 4.0 | 2.4 | 0.0 | 19.7 | 17.7 |
| Nitrobenzene | 19.4 | 7.4 | 2.2 | 0.0 | 15.7 | 22.7 |
| Water | 12.9 | 31.4 | 20.8 | 34.1 | 22.3 | — |

Adapted from Ignat, A. V. and Melder, L. I., *Zh. Prikl. Khim. (Leningrad)*, 60, 1136, 1987; 62, 419, 1989; *J. Appl. Chem. U.S.S.R.*, 60, 1070, 1987; 62, 376, 1989; *Eesti NSV Tead. Akad. Toim. Keem.*, 36(1), 45, 1987.

TABLE 3
Total and Component Cohesion Parameters for Some Lipophilic Liquids

| Liquid | $\delta/\text{MPa}^{1/2}$ | | | | | | |
|---|---------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | δ_a^a | δ_b^b | δ_c^b | δ_d^c | δ_e^d | δ_f^e | δ_g^f |
| Octanoic acid | 16.2 | 0.7 | 0.0 | 1.2 | 11.2 | — | 19.8 |
| 1-Decanol | 16.5 | 2.7 | 0.6 | 5.1 | 11.1 | — | 20.5 |
| 1,2-Propanediyl dinonanoate, propylene glycol dipelargonate | 16.6 | 0.9 | 0.1 | 2.3 | 7.6 | 18.0 | 18.4 |
| Dodecane | 16.1 | 0.0 | 0.0 | 0.0 | 0.0 | — | 16.1 |
| 2-Octyldodecanol | 16.9 | 0.5 | 0.0 | 1.2 | 8.7 | 19.2 | 19.0 |
| Isopropyl tetradecanoate, isopropyl myristate | 16.4 | 0.9 | 0.1 | 2.0 | 5.7 | 17.6 | 17.5 |
| 1,2,3-Propanetriyl trioctanodecanoate, glycerol tricaprylocaprate | 16.8 | 0.8 | 0.1 | 2.2 | 8.2 | 18.0 | 18.8 |

^a Refractive index.

^b Dipole moment and refractive index.

^c $\delta_c^c = \delta_c^c + 2\delta_c \delta_d$

^d $\delta_e^d = \delta_e^d - \delta_e^d - \delta_e^d$

^e Gas-liquid chromatography.

^f Group addition.⁸²

Adapted from Munafo, A., Buchmann, M., Hô Nam-Tran, and Kesselring, U. W., *J. Pharm. Sci.*, 77, 169, 1988.

evaluated the component cohesion parameters for polar liquids, from the activity coefficients of alcohols dissolved in them.

Munafo, Buchmann, Hô Nam-Tran, and Kesselring³⁷ (see Table 3) evaluated for some lipophilic liquids all components, except for separation of δ_a and δ_b , from chromatographic measurements and molecular properties after comparing the various methods, including that of Fedors.⁸²

5.7 EMPIRICAL CORRECTIONS FOR GEOMETRIC MEAN DEVIATIONS

Comparison of the equations in Section 4.2 and 5.6 shows that the original Hildebrand-Scatchard equation can be considered as a simplified form of a more general relationship. Many equations of intermediate simplification also have been used.

One of the specific simplifications in the Hildebrand-Scatchard equation was the use of the geometric mean approximation, Equation 25, and there have been several approaches to the accommodation of deviations from geometric mean behavior. Walker⁸³ proposed the dimensionless specific interchange coefficient, uK , which has values between 0.98 and 1.06 for many liquids,

$${}^u_c = {}^uK ({}^t_c {}^j_c)^{1/2} \quad (26)$$

so

$${}^u_A = {}^t_c + {}^j_c - 2 {}^uK {}^t_c^{1/2} {}^j_c^{1/2} \quad (27)$$

$$= {}^t_\delta^2 + {}^j_\delta^2 - 2 {}^uK {}^t_\delta {}^j_\delta \quad (28)$$

This parameter was given the symbol f by Reed^{84,85} and Sonnich Thomsen⁸⁶⁻⁸⁸ and also divided into several factors corresponding to different correction terms. Prausnitz and co-workers and others⁸⁹⁻⁹³ used the dimensionless constant u_l (with a magnitude on the order of 10^{-2} to 10^{-1}), characteristic of a given pair of materials and almost independent of temperature and composition,

$${}^u_c = ({}^t_c {}^j_c)^{1/2} (1 - {}^u_l) \quad (29)$$

and of course this is related to uK by

$${}^u_l = 1 - {}^uK \quad (30)$$

so the empirical expression for interchange cohesive pressure, Equation 16, becomes

$${}^u_A = ({}^t_\delta - {}^j_\delta)^2 + 2 {}^u_l {}^t_\delta {}^j_\delta \quad (31)$$

from which it is clear that the effect of the correction factor is most pronounced when ${}^t_\delta \approx {}^j_\delta$. Examples are given in Table 4.

Martin et al.⁹⁴⁻⁹⁶ in studies of drug solubilities proposed the binary interaction parameter u_W , which in terms of u_A is defined by

$${}^u_A = ({}^t_\delta^2 + {}^j_\delta^2 - 2 {}^u_W) = ({}^t_\delta - {}^j_\delta)^2 + 2 ({}^t_\delta {}^j_\delta - {}^u_W) \quad (32)$$

They also showed⁹⁷ that these parameters are simply three different representations of deviations from the geometric mean mixing approximation,

$$1 - {}^u_l = {}^u_W / ({}^t_\delta {}^j_\delta) = {}^uK \quad (33a)$$

or

TABLE 4
Binary Interaction Parameters for Solutes in Cryogenic Liquids

| Solute(<i>j</i>)-solvent(<i>i</i>) | η_i | Recommended range for use of given η_i , T/K | Maximum error, $100 x_{obs} - x_{calc} /x_{obs}$ |
|--|----------|---|---|
| Acetylene-carbon dioxide | 0.04 | 170—188 | 5 |
| Acetylene-ethane | 0.11 | 150—177 | 30 |
| Acetylene-ethylene | 0.02 | 100—160 | 25 |
| Acetylene-methane | 0.10 | 105—135 | 40 |
| Acetylene-nitrogen | 0.07 | 77 | — |
| Acetylene-oxygen | 0.18 | 90 | — |
| Argon-methane | 0.00 | 72—83 | 2 |
| Argon-nitrogen | 0.00 | 70—83 | 1 |
| Argon-oxygen | 0.06 | 63—83 | 25 |
| Butane-oxygen | 0.08 | 90 | — |
| Carbon dioxide-acetylene | -0.02 | 175—190 | 3 |
| Carbon dioxide-butane | 0.09 | 140—200 | 20 |
| Carbon dioxide-ethane | 0.08 | 110—170 | 15 |
| Carbon dioxide-ethylene | 0.00 | 140—170 | 10 |
| Carbon dioxide-methane | -0.02 | 110—140 | 10 |
| Carbon dioxide-nitrogen | -0.18 | 77 | — |
| Carbon dioxide-oxygen | 0.03 | 90 | — |
| Carbon dioxide-propane | 0.08 | 120—200 | 10 |
| Carbon dioxide-propylene | 0.01 | 130—210 | 20 |
| Ethane-ethylene | 0.01 | — | — |
| Ethane-oxygen | 0.03 | 60—75 | 20 |
| Ethylene-nitrogen | 0.06 | 70—85 | 35 |
| Ethylene-oxygen | 0.06 | 75—90 | 15 |
| Hydrogen sulfide-butane | 0.05 | 140—170 | 25 |
| Hydrogen sulfide-ethane | 0.07 | 120—160 | 30 |
| Hydrogen sulfide-ethylene | -0.01 | 120—185 | 15 |
| Hydrogen sulfide-methane | 0.04 | 120—150 | 40 |
| Hydrogen sulfide-propane | 0.06 | 140—170 | 45 |
| Hydrogen sulfide-propylene | -0.005 | 130—180 | 5 |
| Methane-ethane | 0.01 | — | — |
| Methane-ethylene | 0.01 | — | — |
| Methane-nitrogen | -0.02 | 70—90 | 5 |
| Methane-oxygen | 0.05 | 70—90 | 3 |
| Nitrogen-hydrogen | 0 | 26—33 | — |
| Nitrogen-oxygen | 0 | — | — |
| Propane-oxygen | 0.02 | 60—70 | 115 |
| Propylene-nitrogen | -0.01 | 65—80 | 75 |
| Propylene-oxygen | 0.05 | 65—75 | 30 |

Adapted from Preston, G. T. and Prausnitz, J. M., *Ind. Eng. Chem. Proc. Des. Dev.*, 9, 264, 1970.

$$\eta^W = \eta^K \eta^{\delta} \eta^{\delta} \quad (33b)$$

Although values of η^K are never very different from unity, these small differences can account for large variations in solubilities.⁹⁸ The application by Martin and co-workers of this geometric mean correction to the Hildebrand-Scatchard equation and polynomial regression to fit complex solutes in various solvents is outlined in Chapter 12. More recently, Li et al.⁹⁹ proposed the parameter $\eta^{\delta'}$ defined such that

$$\eta^{\delta'} = \eta^W{}^{1/2} = (\eta^K \eta^{\delta} \eta^{\delta})^{1/2} = (1 - \eta^I)^{1/2} (\eta^{\delta} \eta^{\delta})^{1/2} \quad (34)$$

which has the advantage that the relationship of this correction parameter to η^{δ} and η^{δ} is clear, and that it retains the cohesion parameter dimensions of (pressure)^{1/2}.

Mikos and Peppas¹⁶⁵ employed the geometric mean correction parameter ${}^i l$ in the correlation of polymer-liquid interaction parameters (Section 13.5) for hydrophilic copolymers with water, using

$$\chi_H = {}^i V / (RT) [({}^i \delta - {}^j \delta)^2 + 2 {}^i l {}^i \delta {}^j \delta]$$

with ${}^i l$ ranging from -0.15 to -0.25 depending on copolymer composition and volume fraction. For example, they obtained -0.25 for poly(methacrylic acid) and -0.18 for poly(2-hydroxyethyl methacrylate) extrapolated to infinite dilution in water at 25°C , values which may be compared with the generally lower magnitudes in Table 4. This parameter is negative for the hydrogels, consistent with specific effects such as hydrogen bonding favoring dissolution.

The virtual Hildebrand parameter ${}^j \Lambda$ (Section 5.5) is related to ${}^i W$ by the parabolic relationship⁷³

$$-2 {}^i W = {}^j \Lambda^2 - 2 {}^i \delta {}^j \Lambda - {}^j \delta^2 \quad (35)$$

The geometric mean corrections ${}^i l$ for systems of testosterone propionate and unsaturated hydrocarbons were found to fit a rectilinear function of the branching ratio of the hydrocarbon liquids, and for related esters there was a good correlation between ${}^i l$ and infrared carbonyl stretching frequencies.¹⁰⁰

It is apparent that ${}^i \delta$, ${}^i l$, ${}^i k$, and ${}^i W$ are binary parameters which depend in a complex manner on many properties of i and j , and are usually determined by empirical means, for example, from liquid phase activity coefficients, when Equation 15, Chapter 4, becomes

$$RT \ln f_x = {}^j V {}^i \phi^2 \{ ({}^i \delta - {}^j \delta)^2 + 2 {}^i l {}^i \delta {}^j \delta \} \quad (36)$$

They also may be determined from gas phase data^{88,92,101-105} where

$${}^i T_c = ({}^i T_c {}^j T_c)^{1/2} (1 - {}^i k) \quad (37)$$

Although the parameters ${}^i l$ and ${}^i k$ are not identical, because the former reflects some liquid phase aspects absent from gas mixtures, they are often of comparable magnitude.

For the particular case of bonding energy E , for polar interactions, Pauling¹⁰⁶ suggested

$${}^i E / \text{kJ mol}^{-1} = ({}^i E {}^j E)^{1/2} / \text{kJ mol}^{-1} + 125(X - {}^j X)^2 \quad (38)$$

where X is the electronegativity. The resulting expression in terms of cohesion pressures is

$${}^i c = ({}^i c {}^j c)^{1/2} + k(X - {}^j X)^2 / ({}^i V {}^j V)^{1/2} \quad (39)$$

where k has been taken as 125 kJ mol^{-1} for intermetallic solutions.¹⁰⁷

The presence of molecular quadrupole moments introduces significant deviations from geometric mean behavior. In analyzing data on the solubility of solid carbon dioxide in liquid hydrocarbons, Myers and Prausnitz^{102,108} calculated the ideal solubility (see Section 12.1) and assumed that the activity coefficient of carbon dioxide (referred to its pure subcooled liquid) was given by Equation 15, Chapter 4:

$$RT \ln f_x = {}^i A {}^j V {}^i \phi^2 \quad (40)$$

where ${}^j V$ is the molar volume of subcooled liquid carbon dioxide, ${}^i \phi$ is the volume fraction of the liquid hydrocarbon, and ${}^i A$ is the interchange cohesive pressure of subcooled liquid

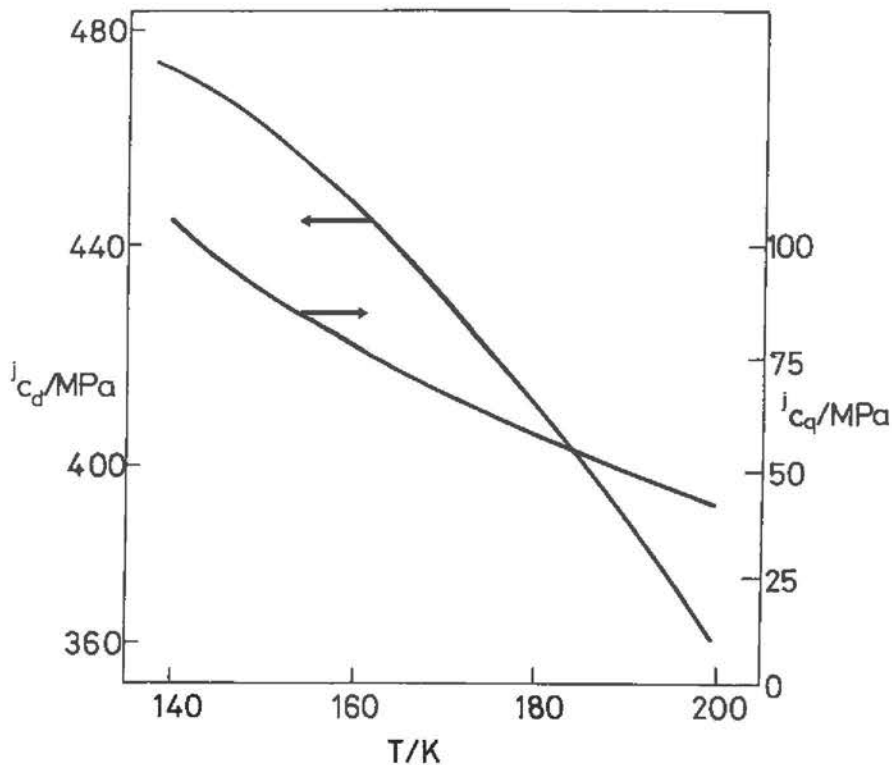


FIGURE 1. Dispersion and quadrupole cohesive pressures of subcooled liquid carbon dioxide as functions of temperature. (Adapted from Myers, A. L. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 4, 209, 1965.)

carbon dioxide with liquid hydrocarbons (Equation 10, Chapter 4). However, since the quadrupole moment of carbon dioxide makes an appreciable contribution to its cohesive pressure, the cohesive pressures were separated into two parts due to dispersion (d) forces and quadrupole (q) forces before the geometric mean approximation was used:

$$j_c = j_{c_d} + j_{c_q} \text{ and } i_c = i_{c_d} + i_{c_q} \quad (41)$$

The relative estimated values of dispersion and quadrupole cohesive pressures for subcooled liquid carbon dioxide are shown in Figure 1 (note the different scales) and the sum (Equation 41) is shown in Figure 2. In mixtures, the geometric mean approximation retained for the dispersion interactions, u_{c_d} was evaluated from theoretical expressions, and the total cohesive pressure was given by

$$u_c = (i_{c_d} j_{c_d})^{1/2} + u_{c_q} + u_{c_{ab}} \quad (42)$$

The last term is a measure of the tendency of carbon dioxide (with Lewis acid properties) to complex with unsaturated hydrocarbons, and was evaluated by difference (Figure 3). Since the complex formation is exothermic, $u_{c_{ab}}$ rises with falling temperature and becomes relatively more important in such low temperature systems. The full expression for the interchange cohesive pressure is thus

$$\begin{aligned} u_A &= i_c + j_c - 2 u_c \\ &= i_c + j_c - 2 [(i_{c_d} j_{c_d})^{1/2} + u_{c_q}] \end{aligned} \quad (43)$$

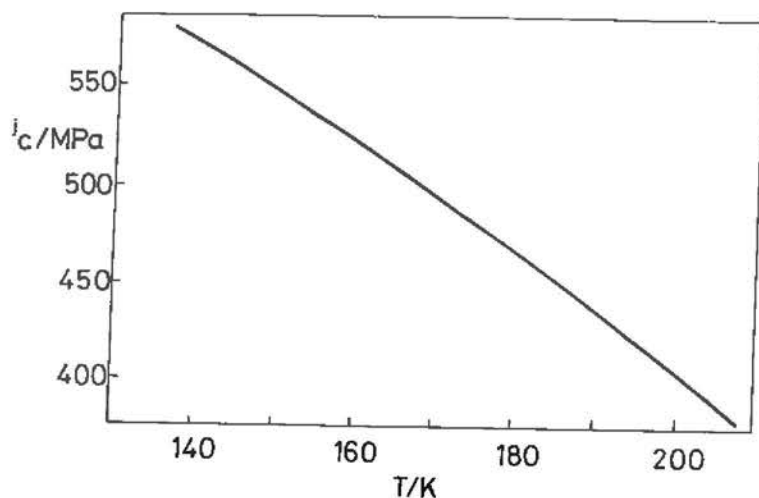


FIGURE 2. Cohesive pressure of subcooled liquid carbon dioxide as a function of temperature. (Adapted from Myers, A. L. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 4, 209, 1965.)

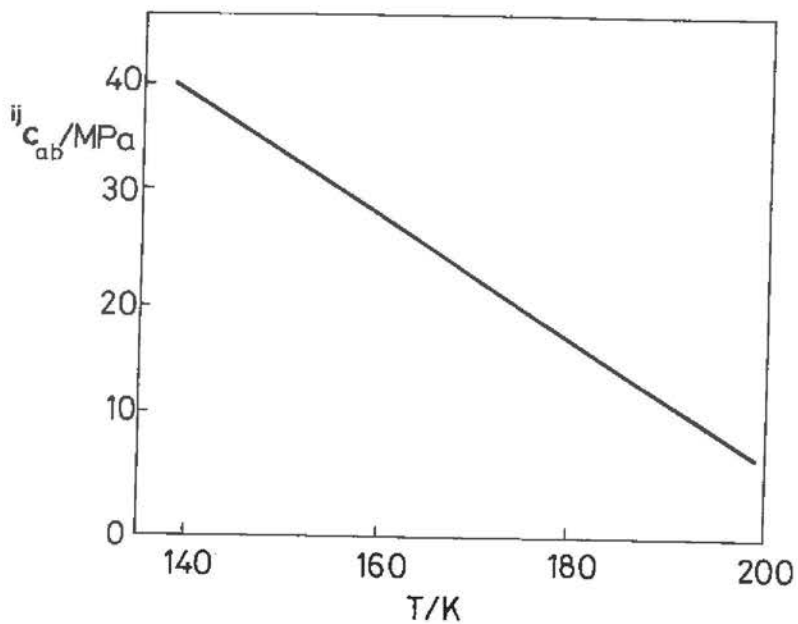


FIGURE 3. Acid-base complex contribution to the cohesive pressure of carbon dioxide-alkene mixtures as a function of temperature. (Adapted from Myers, A. L. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 4, 209, 1965.)

5.8 POLAR-NONPOLAR COHESION PARAMETERS

Van Arkel,³⁶ Small,⁶⁰ and Prausnitz and co-workers^{102,109-114} divided the total cohesion parameter into two main components, defining a nonpolar cohesion parameter (δ_n) and a polar parameter (δ_p). Although this tends to neglect induction interactions, these may be taken care of by an additional parameter. More of a problem from a practical point of view is the omission of specific interactions. Polar-nonpolar parameters are related to the Hildebrand parameter (total cohesion parameter) by

$$\delta^2 = \delta_n^2 + \delta_p^2 \quad (44)$$

and comparison with Equation 24 suggests that δ_n can be identified with δ_d and that δ_p corresponds to δ_e .

In their evaluation of δ_n and δ_p for polar liquids, Blanks and Prausnitz¹¹⁰ used the homomorph concept. This is discussed in Section 6.7, but basically it is a method which assumes that the polar energy of vaporization is the difference between the experimentally determined total energy of vaporization and the energy of vaporization of a nonpolar liquid having molecules very nearly the same size and shape as those of the polar liquid. Tables 5a and 5b list those polar and nonpolar cohesion parameter values.

Weimer and Prausnitz^{111,113} also published values of polar and nonpolar cohesion parameters for polar liquids; again alcohols and acids were omitted because of their strong hydrogen-bonding properties (Tables 6 and 7). These parameters, evaluated at several temperatures, used homomorph data (Figures 6 to 8, Chapter 6) which were rather different from those of Blanks and Prausnitz, and the numerical values differ slightly. Yet another set of values was presented by Helpinstill and Van Winkle¹¹⁵ (Tables 8 and 9).

These polar-nonpolar cohesion parameters can be used in a similar way to Hildebrand parameters to evaluate the interchange cohesion pressure, and from this the derived quantities such as energy of mixing. All three sets of data have been tabulated here because each set is still in use, and as stressed in Section 6.10, it is essential to use self-consistent sets of cohesion parameters. Their application to various systems is now summarized, first for nonpolar-nonpolar systems, then for polar-nonpolar and polar-polar systems.

For a mixture of *nonpolar* liquids (i.e., when only dispersion forces occur),

$${}^i u_A = {}^i c + {}^j c - 2 {}^i u_c = {}^i \delta_n^2 + {}^j \delta_n^2 - 2 {}^i \delta_n {}^j \delta_n \quad (45)$$

$$= ({}^i \delta_n - {}^j \delta_n)^2 = ({}^i \delta - {}^j \delta)^2 \quad (46)$$

as used in Equation 13, Chapter 4.

For interaction between a *polar* substance (*i*) and a *nonpolar* substance (*j*), a term ${}^i u_\Psi$ is included for the *i-j* induction pressure, so the expression for the interchange cohesive pressure is

$${}^i u_A = {}^i c + {}^j c - 2 {}^i u_c = {}^i \delta_n^2 + {}^i \delta_p^2 + {}^j \delta_n^2 - 2 ({}^i \delta_n {}^j \delta_n + {}^i u_\Psi) \quad (47)$$

$$= ({}^i \delta_n - {}^j \delta_n)^2 + {}^i \delta_p^2 - 2 {}^i u_\Psi \quad (48)$$

As indicated in Equation 4, Chapter 3, the orientation energy (unlike the induction and dispersion energies) has a temperature dependence, so Equation 48 should reflect this, and a more complete expression is

TABLE 5a
Molar Volumes and Hildebrand Parameters of
Nonpolar Liquids at 25°C

| Liquid | $V/\text{cm}^3 \text{ mol}^{-1}$ | $\delta/\text{MPa}^{1/2}$ |
|-----------------------------------|----------------------------------|---------------------------|
| Alkanes | | |
| Methane | 53 ^a | 9.6 ^a |
| Ethane | 69 ^a | 11.6 ^a |
| Propane | 85 ^a | 12.7 ^a |
| Butane | 101.4 | 13.5 |
| Isobutane, 2-methylpropane | 105.5 | 12.8 |
| Pentane | 116.1 | 14.3 |
| Isopentane, 2-methylbutane | 117.4 | 13.8 |
| Neopentane, 2,2-dimethylpropane | 123.3 | 12.5 |
| Hexane | 131.6 | 14.8 |
| Heptane | 147.5 | 15.2 |
| 2,2,3-Trimethylbutane | 146.1 | 14.2 |
| Octane | 163.5 | 15.5 |
| Isooctane, 2,2,4-trimethylpentane | 166.1 | 14.0 |
| Nonane | 179.7 | 15.6 |
| Decane | 195.9 | 15.8 |
| Dodecane | 228.6 | 16.0 |
| Tetradecane | 261.3 | 16.2 |
| Hexadecane | 294.1 | 16.3 |
| Octadecane | 326.9 | 16.4 |
| Eicosane | 359.8 | 16.5 |
| Alkenes | | |
| Ethylene | 63 ^a | 11.3 ^a |
| Propylene | 79 ^a | 12.5 ^a |
| 1-Butylene | 95.3 | 13.7 |
| <i>cis</i> -2-Butylene | 91.2 | 14.7 |
| <i>trans</i> -2-Butylene | 93.8 | 14.3 |
| Isobutylene, 2-methylpropene | 95.4 | 13.7 |
| 1,3-Butadiene | 88.0 | 14.5 |
| Isoprene | 100.8 | 15.2 |
| Cycloalkanes | | |
| Cyclopentane | 94.7 | 16.6 |
| Cyclohexane | 108.7 | 16.7 |
| Methylcyclohexane | 128.3 | 16.0 |

TABLE 5a (continued)
Molar Volumes and Hildebrand Parameters of
Nonpolar Liquids at 25°C

| Liquid | V/cm ³ mol ⁻¹ | δ/MPa ^{1/2} |
|---|-------------------------------------|----------------------|
| Aromatics | | |
| Benzene | 89.4 | 18.7 |
| Toluene, methylbenzene | 106.9 | 18.2 |
| Ethylbenzene | 123.1 | 18.0 |
| <i>o</i> -Xylene, 1,2-dimethylbenzene | 121.2 | 18.4 |
| <i>m</i> -Xylene, 1,3-dimethylbenzene | 123.5 | 18.0 |
| <i>p</i> -Xylene, 1,4-dimethylbenzene | 123.9 | 17.9 |
| Propylbenzene | 140.1 | 17.7 |
| Mesitylene, 1,3,5-trimethylbenzene | 140 | 18.0 |
| Styrene, ethenylbenzene | 115.6 | 19.0 |
| Tetrahydronaphthalene, tetralin | — | 19.4 |
| Tetrachloromethane, carbon tetra- chloride | 97.1 | 17.6 |

* Estimated from gas solubility data.¹¹⁴

Adapted from Blanks, R. F. and Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, 3, 1, 1964.

$${}^uA = ({}^i\delta_\lambda - {}^j\delta_\lambda)^2 + (T_j/T) {}^i\delta_\tau^2 - 2{}^u\Psi \quad (49)$$

where T_j is the temperature at which the polar parameter ${}^i\delta_\tau$ was obtained. The tables in this section show that δ_λ also varies with temperature, but to a smaller extent, and an alternative (and preferred) procedure is to evaluate all cohesion parameters at the temperatures at which they will be used.

Theory suggests that the induction term, ${}^u\Psi$, should depend on the product ${}^j\delta_\lambda {}^i\delta_\tau$, where ${}^j\delta_\lambda$ is the cohesion parameter of the nonpolar component. When evaluated experimentally by difference¹¹⁰ the correlation in Figure 4 was observed. Weimer^{102,111,113} found that activity coefficient data (Section 7.5) for infinitely dilute solutions of hydrocarbons (j) in polar liquids (i) could be correlated well by expressing the induction parameter ${}^u\Psi$ as proportional to the square of the polar cohesion parameter ${}^i\delta_\tau^2$:

- For linear and cyclic alkanes, ${}^u\Psi = 0.40 {}^i\delta_\tau^2$
- For the alkene 1-pentene, ${}^u\Psi = 0.42 {}^i\delta_\tau^2$
- For the aromatic hydrocarbon benzene, ${}^u\Psi = 0.45 {}^i\delta_\tau^2$

In other words, this empirical induction cohesive pressure term is related to the polar cohesive pressure of the polar liquid and to the *class* of the hydrocarbon, but is not directly dependent on the cohesive pressure of the hydrocarbon. Weimer and Prausnitz¹¹³ explained this on the basis of the polar molecule interacting with only one carbon-carbon bond during a collision, so the interchange cohesive pressure depends on the polarizability of the carbon-carbon bond, which increases in the order

single bond, C-C < double bond, C = C < aromatic

Although these correlations were obtained in conditions of high concentrations of the polar component and therefore are expected to be of limited applicability, they provide a simple method of screening polar liquids for use in hydrocarbon separations. For example, the

TABLE 5b
Molar Volumes, Nonpolar Cohesion Parameters, and Polar Cohesion Parameters of Polar Liquids at 25°C

| Liquids | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_p/\text{MPa}^{1/2}$ | Polar, $\delta_s/\text{MPa}^{1/2}$ | Homomorph |
|---|--------------------------------|--|---------------------------------------|---------------------|
| Halogen Compounds | | | | |
| Trichloromethane, chloroform | 80.7 | 15.8 | 10.0 | Figure 5, Chapter 6 |
| Chloroethane, ethyl chloride | 73 | 14.9 | 9.0 | Figure 5, Chapter 6 |
| 1,2-Dichloroethane, ethylene dichloride | 79.4 | 16.1 | 11.9 | Figure 5, Chapter 6 |
| 1,1-Dichloroethane | 84.8 | 15.5 | 10.3 | Isobutane |
| 1,1,1-Trichloroethane | 100.4 | 15.8 | 8.9 | Neopentane |
| Trichloroethylene | 90.2 | 16.3 | 9.6 | Isopentane |
| 1,2-Dibromoethane | 87 | 16.9 | 13.0 | Figure 5, Chapter 6 |
| Chlorobenzene | 102.1 | 18.9 | 6.0 | Toluene |
| Ketones | | | | |
| Acetone, 2-propanone | 74.0 | 15.5 | 12.5 | Figure 5, Chapter 6 |
| Methyl ethyl ketone, 2-butanone | 90.2 | 15.9 | 10.3 | Figure 5, Chapter 6 |
| Methyl propyl ketone | 107.5 | 15.8 | 9.1 | |
| Methyl isobutyl ketone | 125.8 | 15.3 | 8.5 | Isohexane |
| Methyl amyl ketone | 140.8 | 15.9 | 8.6 | Figure 5, Chapter 6 |
| Dipropyl ketone | 140.7 | 15.8 | 8.8 | Figure 5, Chapter 6 |
| Hexamethyl ketone | 157.5 | 15.9 | 8.4 | Figure 5, Chapter 6 |
| Mesityl oxide | 115.6 | 17.1 | 7.8 | 2-Methylpentene |
| Esters | | | | |
| Ethyl acetate | 98.5 | 15.2 | 10.6 | Figure 5, Chapter 6 |
| Propyl acetate | 115.7 | 15.6 | 8.8 | Figure 5, Chapter 6 |
| Butyl acetate | 132.5 | 15.6 | 8.7 | Figure 5, Chapter 6 |
| Amyl acetate, pentyl acetate | 148.9 | 15.6 | 8.6 | Figure 5, Chapter 6 |
| Ethyl propionate | 115.5 | 15.6 | 9.2 | Figure 5, Chapter 6 |
| Ethers | | | | |
| Diethyl ether | 104.8 | 14.3 | 4.6 | Figure 5, Chapter 6 |
| Methyl isopropyl ether | 103.8 | 14.4 | 5.5 | Isobutane |
| 1,4-Dioxane | 85.7 | 17.5 | 9.5 | Cyclopentane |
| Miscellaneous | | | | |
| Nitropropane | 90.4 | 16.4 | 13.4 | Figure 5, Chapter 6 |
| Acetonitrile | 52.9 | 16.2 | 18.0 | Figure 5, Chapter 6 |
| Propionitrile | 70.3 | 16.3 | 14.7 | Figure 5, Chapter 6 |

Adapted from Blanks, R. F. and Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, 3, 1, 1964.

ability of a solvent to "distinguish" between a saturated hydrocarbon and an unsaturated hydrocarbon depends primarily on the solvent having a large cohesive pressure (large cohesive energy and small molar volume).

In systems where *both components are polar*, induction interactions may be considered to be negligibly small in comparison with dipole-dipole interactions. If specific interactions are also negligible, the interchange cohesive pressure is

TABLE 6
Molar Volumes and Nonpolar Cohesion Parameters of
Hydrocarbons at Various Temperatures

| Liquid | $t^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | $\delta_v/\text{MPa}^{1/2}$ |
|---------------------------------------|---------------------|--------------------------------|-----------------------------|
| Propane | 25 | 89.5 | 13.4 |
| Butane | 25 | 101.4 | 14.2 |
| Pentane | 0 | 111.8 | 15.2 |
| | 25 | 116.2 | 14.7 |
| | 45 | 120.3 | 14.2 |
| Hexane | 0 | 127.3 | 15.6 |
| | 25 | 131.6 | 15.0 |
| | 45 | 135.4 | 14.5 |
| | 60 | 138.7 | 14.2 |
| | 100 | 148.0 | 13.4 |
| Heptane | 25 | 147.4 | 15.3 |
| | 60 | 154.3 | 14.5 |
| | 100 | 164.0 | 13.6 |
| Decane | 25 | 195.9 | 16.1 |
| | 60 | 203.4 | 15.1 |
| | 100 | 213.0 | 14.2 |
| Hexadecane | 25 | 294.1 | 17.9 |
| | 60 | 303.6 | 16.4 |
| | 100 | 315.4 | 15.1 |
| Cyclopentane | 25 | 94.7 | 16.8 |
| Methylcyclopentane | 25 | 113.1 | 16.2 |
| Cyclohexane | 0 | 105.6 | 17.5 |
| | 25 | 108.7 | 16.8 |
| | 45 | 111.5 | 16.4 |
| | 60 | 113.6 | 16.0 |
| | 100 | 119.4 | 15.2 |
| Methylcyclohexane | 0 | 124.8 | 16.7 |
| | 25 | 128.3 | 16.1 |
| | 45 | 131.3 | 15.6 |
| | 60 | 133.7 | 15.3 |
| | 100 | 140.4 | 14.5 |
| Ethylcyclohexane | 25 | 143.1 | 16.4 |
| | 60 | 148.5 | 15.6 |
| 1-Butene | 25 | 95.3 | 14.5 |
| 1-Pentene | 0 | 106.1 | 15.4 |
| | 25 | 110.4 | 14.8 |
| | 45 | 113.1 | 14.4 |
| 1,3-Butadiene | 25 | 88.0 | 15.2 |
| Benzene | 25 | 89.4 | 18.8 |
| | 45 | 91.7 | 18.3 |
| | 60 | 93.4 | 17.9 |
| | 100 | 98.8 | 16.9 |
| Toluene, methylbenzene | 25 | 106.8 | 18.3 |
| | 45 | 109.2 | 17.8 |
| | 60 | 111.0 | 17.4 |
| | 100 | 116.2 | 16.6 |
| Ethylbenzene | 25 | 123.1 | 18.4 |
| <i>p</i> -Xylene, 1,4-dimethylbenzene | 25 | 123.9 | 18.1 |
| Mesitylene, 1,3,5-trimethylbenzene | 25 | 139.6 | 18.2 |

Adapted from Weimer, R. F. and Prausnitz, J. M., *Hydrocarbon Process. Petr. Ref.*, 44, 237, 1965.

TABLE 7
Molar Volumes, Nonpolar Cohesion Parameters, and Polar Cohesion Parameters of Polar Liquids at Various Temperatures in Order of Increasing Polarity

| Liquid | $t/^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_x/\text{MPa}^{1/2}$ | Polar, $\delta_p/\text{MPa}^{1/2}$ |
|---------------------------------|----------------------|--------------------------------|--|---------------------------------------|
| Acetophenone | 25 | 117.4 | 19.3 | 7.6 |
| Tetrahydrofuran | 0 | 79.3 | 17.6 | 7.9 |
| | 25 | 81.7 | 17.0 | 7.6 |
| | 45 | 85.0 | 16.5 | 7.1 |
| Pyridine | 25 | 80.9 | 20.2 | 7.6 |
| | 60 | 83.9 | 19.1 | 7.8 |
| | 100 | 87.4 | 18.1 | 8.0 |
| Cyclohexanone | 25 | 104.2 | 18.1 | 8.3 |
| Chloroethane | 25 | 74.1 | 15.1 | 8.8 |
| Diethyl ketone, 3-pentanone | 0 | 103.3 | 16.4 | 9.3 |
| | 25 | 106.4 | 15.9 | 9.1 |
| | 45 | 108.9 | 15.4 | 8.9 |
| | 60 | 110.7 | 15.1 | 8.8 |
| | 100 | 116.1 | 14.4 | 8.5 |
| Diethyl carbonate | 25 | 121.9 | 16.1 | 9.2 |
| Bromoethane | 25 | 75.1 | 15.6 | 9.9 |
| | 45 | 77.3 | 15.2 | 9.5 |
| Nitrobenzene | 25 | 102.7 | 19.8 | 10.0 |
| Di-(2-chloroethyl) ether | 0 | 109.7 | 17.8 | 11.7 |
| | 25 | 117.8 | 17.1 | 10.7 |
| Trimethyl phosphate | 25 | 116.2 | 17.3 | 10.7 |
| Iodoethane | 25 | 81.1 | 15.7 | 10.7 |
| | 45 | 83.0 | 15.2 | 10.5 |
| Methyl ethyl ketone, 2-butanone | 0 | 87.3 | 16.2 | 11.3 |
| | 25 | 90.1 | 15.6 | 10.9 |
| | 45 | 92.6 | 15.2 | 10.6 |
| | 60 | 94.5 | 14.9 | 10.4 |
| | 100 | 99.9 | 14.1 | 10.0 |
| Cyclopentanone | 25 | 89.5 | 17.8 | 11.0 |
| 2,4-Pentanedione | 25 | 103.0 | 16.5 | 11.6 |
| 2,5-Hexanedione, acetylacetone | 25 | 117.7 | 17.3 | 12.0 |
| Diethyl oxalate | 0 | 132.7 | 17.8 | 12.3 |
| | 25 | 136.2 | 17.1 | 12.1 |
| | 45 | 139.3 | 16.6 | 12.1 |
| 2-Nitropropane | 25 | 90.7 | 16.3 | 12.3 |
| Methoxyacetone | 25 | 93.2 | 16.2 | 12.5 |
| | 45 | 96.0 | 15.5 | 12.1 |
| Acetone, 2-propanone | 0 | 72.3 | 16.2 | 12.9 |
| | 25 | 74.0 | 15.7 | 12.6 |
| | 45 | 76.2 | 15.2 | 12.2 |
| | 60 | 78.1 | 15.0 | 11.9 |
| | 100 | 83.4 | 14.1 | 11.2 |
| Dimethyl carbonate | 25 | 85.0 | 15.9 | 12.7 |
| Butyronitrile | 0 | 85.4 | 16.8 | 13.3 |
| | 25 | 87.9 | 16.3 | 12.8 |
| | 45 | 90.1 | 15.9 | 12.6 |
| 2,3-Butanedione, diacetyl | 25 | 87.8 | 15.8 | 13.0 |
| | 45 | 90.4 | 15.4 | 12.6 |
| Aniline | 25 | 91.5 | 20.1 | 13.0 |
| | 60 | 94.3 | 19.2 | 12.8 |
| | 100 | 97.9 | 18.3 | 12.7 |
| 1-Nitropropane | 25 | 89.5 | 16.5 | 13.1 |
| N-Methyl-2-pyrrolidone | 25 | 96.6 | 18.7 | 13.4 |

TABLE 7 (continued)
Molar Volumes, Nonpolar Cohesion Parameters, and Polar Cohesion Parameters of Polar Liquids at Various Temperatures in Order of Increasing Polarity

| Liquid | $t/^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_v/\text{MPa}^{1/2}$ | Polar, $\delta_p/\text{MPa}^{1/2}$ |
|-------------------------------|----------------------|--------------------------------|--|---------------------------------------|
| Acetic anhydride | 25 | 95.0 | 16.1 | 14.5 |
| Propionitrile | 0 | 68.7 | 16.9 | 15.2 |
| | 25 | 70.9 | 16.3 | 14.7 |
| | 45 | 72.9 | 15.9 | 14.2 |
| | 60 | 74.4 | 15.6 | 13.9 |
| | 100 | 79.0 | 14.9 | 13.2 |
| Citraconic anhydride | 25 | 89.7 | 19.3 | 14.8 |
| Methoxyacetonitrile | 25 | 75.2 | 16.5 | 15.0 |
| Furfural | 0 | 81.4 | 19.2 | 15.9 |
| | 25 | 83.2 | 18.5 | 15.6 |
| | 45 | 84.8 | 18.0 | 15.1 |
| | 60 | 85.9 | 17.7 | 15.2 |
| | 100 | 89.4 | 16.9 | 14.6 |
| Nitroethane | 25 | 72.1 | 16.4 | 15.7 |
| | 45 | 73.6 | 16.1 | 15.3 |
| <i>N,N</i> -Dimethylacetamide | 0 | 90.7 | 17.6 | 16.2 |
| | 25 | 93.2 | 17.0 | 15.7 |
| | 45 | 95.3 | 16.5 | 15.4 |
| γ -Butyrolactone | 25 | 77.1 | 19.4 | 16.4 |
| <i>N,N</i> -Dimethylformamide | 0 | 75.5 | 17.5 | 17.0 |
| | 25 | 77.4 | 17.0 | 16.5 |
| | 45 | 79.0 | 16.5 | 16.2 |
| | 60 | 80.2 | 16.2 | 15.9 |
| | 100 | 83.8 | 15.5 | 15.3 |
| 3-Chloropropionitrile | 25 | 77.7 | 17.3 | 17.9 |
| Acetonitrile | 0 | 51.1 | 16.9 | 19.1 |
| | 25 | 52.6 | 16.4 | 18.4 |
| | 45 | 54.4 | 16.1 | 17.7 |
| | 60 | 55.5 | 15.8 | 17.3 |
| | 100 | 58.9 | 15.1 | 16.3 |
| Ethylenediamine | 25 | 67.3 | 16.6 | 19.2 |
| | 60 | 69.7 | 15.9 | 18.5 |
| Nitromethane | 100 | 72.9 | 15.2 | 17.7 |
| | 25 | 54.3 | 16.5 | 19.3 |
| | 45 | 55.3 | 16.2 | 18.9 |
| Dimethylsulfoxide | 60 | 56.3 | 15.9 | 18.5 |
| | 100 | 59.3 | 15.2 | 17.6 |
| | 25 | 71.3 | 17.5 | 19.4 |

Adapted from Weimer, R. F. and Prausnitz, J. M., *Hydrocarbon Process. Petr. Ref.*, 44, 237, 1965.

$${}^i u_A = ({}^i \delta_\lambda - {}^j \delta_\lambda)^2 + ({}^i \delta_\tau - {}^j \delta_\tau)^2 \quad (50)$$

or, taking the effect of temperature into account as in Equation 49,

$${}^i u_A = ({}^i \delta_\lambda - {}^j \delta_\lambda)^2 + (T^*/T)({}^i \delta_\tau - {}^j \delta_\tau)^2 \quad (51)$$

Helpinstill and Van Winkle¹¹⁵ extended the correlation of Weimer and Prausnitz¹¹³ to polar-polar situations, defining the new parameter ${}^i u_\psi$ to include both polar-polar and polar-nonpolar systems:

TABLE 8
Molar Volumes, Nonpolar Cohesion Parameters and Polar Cohesion
Parameters of Hydrocarbons at Various Temperatures

| Liquid | $t/^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_d/\text{MPa}^{1/2}$ | Polar, $\delta_p/\text{MPa}^{1/2}$ |
|------------------|----------------------|--------------------------------|--|---------------------------------------|
| Propane | 0 | 83.1 | 14.2 | 0.0 |
| | 25 | 89.4 | 13.4 | 0.0 |
| Butane | 0 | 96.7 | 14.8 | 0.0 |
| | 25 | 101.4 | 14.2 | 0.0 |
| | 45 | 106.0 | 13.8 | 0.0 |
| 1-Butene | 0 | 90.3 | 14.8 | 2.9 |
| | 25 | 95.3 | 14.1 | 2.7 |
| Pentane | 0 | 111.8 | 15.3 | 0.0 |
| | 25 | 116.1 | 14.6 | 0.0 |
| | 45 | 120.3 | 14.2 | 0.0 |
| | 60 | 122.9 | 13.9 | 0.0 |
| 1-Pentene | 100 | 131.4 | 13.5 | 0.0 |
| | 0 | 106.0 | 15.4 | 2.5 |
| | 25 | 110.1 | 14.8 | 2.2 |
| | 45 | 113.0 | 14.4 | 2.1 |
| | 60 | 115.9 | 14.0 | 1.9 |
| Hexane | 100 | 121.6 | 13.5 | 1.5 |
| | 0 | 127.3 | 15.5 | 0.0 |
| | 25 | 131.6 | 15.0 | 0.0 |
| | 45 | 135.4 | 14.5 | 0.0 |
| | 60 | 138.7 | 14.2 | 0.0 |
| 1-Hexene | 100 | 148.0 | 13.5 | 0.0 |
| | 0 | 121.6 | 15.7 | 2.1 |
| | 25 | 125.9 | 15.1 | 1.9 |
| | 45 | 129.5 | 14.7 | 1.7 |
| | 60 | 132.4 | 14.3 | 1.6 |
| Heptane | 100 | 140.7 | 13.7 | 1.3 |
| | 0 | 143.8 | 15.9 | 0.0 |
| | 25 | 147.4 | 15.3 | 0.0 |
| | 45 | 151.9 | 14.8 | 0.0 |
| | 60 | 154.3 | 14.5 | 0.0 |
| 1-Heptene | 100 | 164.0 | 13.7 | 0.0 |
| | 45 | 145.5 | 14.8 | 1.4 |
| | 60 | 148.4 | 14.6 | 1.3 |
| Decane | 100 | 156.8 | 13.9 | 0.9 |
| Cyclopentane | 25 | 195.8 | 15.8 | 0.0 |
| | 0 | 91.9 | 17.4 | 0.0 |
| | 25 | 94.7 | 16.8 | 0.0 |
| | 45 | 97.4 | 16.1 | 0.0 |
| | 60 | 99.4 | 15.8 | 0.0 |
| Cyclohexane | 100 | 105.2 | 14.9 | 0.0 |
| | 0 | 105.5 | 17.3 | 0.0 |
| | 25 | 108.7 | 16.6 | 0.0 |
| | 45 | 111.5 | 16.1 | 0.0 |
| | 60 | 113.6 | 15.8 | 0.0 |
| Ethylcyclohexane | 100 | 119.4 | 14.9 | 0.0 |
| Butylcyclohexane | 25 | 143.3 | 16.2 | 0.7 |
| Benzene | 25 | 176.4 | 16.1 | 0.6 |
| | 0 | 86.9 | 19.6 | 0.0 |
| | 25 | 89.4 | 18.8 | 0.0 |
| | 45 | 91.6 | 18.2 | 0.0 |
| | 60 | 93.4 | 18.3 | 0.0 |
| Ethylbenzene | 100 | 98.8 | 17.0 | 0.0 |
| | 25 | 123.1 | 18.1 | 0.4 |

TABLE 8 (continued)
Molar Volumes, Nonpolar Cohesion Parameters and Polar Cohesion Parameters of Hydrocarbons at Various Temperatures

| Liquid | $t/^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_d/\text{MPa}^{1/2}$ | Polar, $\delta_p/\text{MPa}^{1/2}$ |
|---------------------------------------|----------------------|--------------------------------|--|---------------------------------------|
| Butylbenzene | 25 | 156.8 | 18.0 | 0.3 |
| <i>p</i> -Xylene, 1,4-dimethylbenzene | 0 | 121.0 | 18.8 | 0.0 |
| | 25 | 123.9 | 18.1 | 0.0 |
| | 45 | 126.8 | 17.5 | 0.0 |
| | 60 | 128.7 | 17.1 | 0.0 |
| | 100 | 134.1 | 16.4 | 0.0 |
| Mesitylene, 1,3,5-trimethylbenzene | 0 | 136.5 | 19.1 | 0.0 |
| | 25 | 139.8 | 18.0 | 0.0 |
| | 45 | 142.7 | 17.5 | 0.0 |
| | 60 | 144.8 | 17.1 | 0.0 |
| | 100 | 150.8 | 16.3 | 0.0 |
| 1,4-Diethylbenzene | 0 | 153.1 | 18.7 | 0.0 |
| | 25 | 156.9 | 17.9 | 0.0 |
| | 45 | 159.8 | 17.4 | 0.0 |
| | 60 | 162.0 | 17.0 | 0.0 |
| | 100 | 168.6 | 16.2 | 0.0 |
| Toluene, methylbenzene | 0 | 104.0 | 19.0 | 1.7 |
| | 25 | 106.8 | 18.2 | (1.4) |
| | 45 | 109.2 | 17.8 | 1.3 |
| | 60 | 110.8 | 17.4 | 1.2 |
| | 100 | 115.9 | 16.6 | 1.0 |

Adapted from Helpinstill, J. G. and Van Winkle, M., *Ind. Eng. Chem. Proc. Des. Dev.*, 7, 213, 1968.

$${}^uA = ({}^i\delta_r - {}^j\delta_d)^2 + ({}^i\delta_r - {}^j\delta_p)^2 - 2 {}^u\psi \quad (52a)$$

Following a procedure similar to that of Weimer and Prausnitz, they used activity coefficient data for hydrocarbons in polar systems and evaluated the parameter ${}^u\psi$ by difference. It was found to be a linear function of $({}^i\delta_r - {}^j\delta_r)^2$,

- For alkanes, ${}^u\psi = 0.40 ({}^i\delta_r - {}^j\delta_r)^2$
- For the alkene, 1-pentene, ${}^u\psi = 0.22 ({}^i\delta_r - {}^j\delta_r)^2$
- For aromatic hydrocarbons, ${}^u\psi = 0.48 ({}^i\delta_r - {}^j\delta_r)^2$

It follows from this form of the dependence of ${}^u\psi$ on δ_r that Equation 52a can be rewritten as²⁵

$${}^uA = ({}^i\delta_d - {}^j\delta_d)^2 + {}^ub ({}^i\delta_r - {}^j\delta_r)^2 \quad (52b)$$

Values found for the induction cohesive pressure correction factor ub in various situations are listed in Table 10. These examples are not all strictly comparable, but the departure from unity gives an idea of the extent of "correction" necessary as a result of the simple model used.

In terms of the component parameters in Equation 22 (Section 5.6), the induction parameter may be expressed

$${}^u\Psi = {}^i\delta_i {}^j\delta_d + {}^i\delta_d {}^j\delta_i + {}^i\delta_o {}^j\delta_o \quad (53)$$

TABLE 9
Molar Volumes, Nonpolar Cohesion Parameters and Polar Cohesion
Parameters of Polar Liquids at Various Temperatures

| Liquid | $t/^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_d/\text{MPa}^{1/2}$ | Polar, $\delta_p/\text{MPa}^{1/2}$ |
|-------------------------------|----------------------|--------------------------------|--|---------------------------------------|
| Acetone, 2-propanone | 0 | 72.3 | 16.1 | 12.9 |
| | 25 | 74.0 | 15.7 | 12.3 |
| | 45 | 76.2 | 15.2 | 11.9 |
| | 60 | 78.1 | 14.9 | 12.8 |
| | 100 | 83.4 | 14.2 | 10.9 |
| Acetonitrile | 0 | 51.1 | 16.9 | 19.0 |
| | 25 | 52.6 | 16.4 | 18.2 |
| | 45 | 54.4 | 16.0 | 17.5 |
| | 60 | 55.5 | 15.8 | 17.3 |
| | 100 | 58.9 | 15.1 | 16.3 |
| Acetophenone | 0 | 115.0 | 20.3 | 10.1 |
| | 25 | 117.4 | 19.6 | 8.1 |
| | 45 | 119.8 | 19.0 | 8.0 |
| Aniline | 25 | 91.5 | 20.1 | 13.5 |
| | 60 | 94.3 | 19.1 | 13.7 |
| | 100 | 97.9 | 18.2 | 12.2 |
| 1-Butanol | 25 | 92.8 | 15.9 | 17.2 |
| Butyl acetate | 25 | 131.5 | 15.6 | 7.0 |
| γ -Butyrolactone | 25 | 77.0 | 19.6 | 15.4 |
| Butyronitrile | 0 | 85.4 | 16.9 | 12.8 |
| | 25 | 87.9 | 16.3 | 12.4 |
| | 45 | 90.1 | 15.9 | 12.1 |
| Chloropropionitrile | 0 | 75.5 | 17.8 | 19.8 |
| | 25 | 77.7 | 17.2 | 18.7 |
| | 45 | 79.7 | 16.8 | 18.0 |
| Cyclopentanone | 25 | 89.2 | 18.2 | 9.4 |
| Diethyl carbonate | 0 | 118.6 | 16.7 | 9.6 |
| | 25 | 121.9 | 16.1 | 9.0 |
| | 45 | 124.8 | 15.6 | 8.8 |
| Diethyl ketone, 3-pentanone | 0 | 103.3 | 16.4 | 10.4 |
| | 25 | 106.4 | 15.8 | 9.8 |
| | 45 | 108.9 | 15.4 | 9.4 |
| Diethyl oxalate | 0 | 132.7 | 17.9 | 13.0 |
| | 25 | 136.2 | 16.6 | 13.2 |
| | 45 | 139.3 | 16.1 | 12.8 |
| <i>N,N</i> -Dimethylacetamide | 0 | 90.7 | 17.6 | 16.1 |
| | 25 | 93.2 | 16.9 | 14.8 |
| | 45 | 95.3 | 16.5 | 14.2 |
| <i>N,N</i> -Dimethylformamide | 0 | 75.5 | 17.7 | 16.1 |
| | 25 | 77.4 | 17.1 | 15.5 |
| | 45 | 79.0 | 16.6 | 14.9 |
| | 60 | 80.2 | 16.3 | 15.2 |
| | 100 | 83.8 | 15.6 | 14.2 |
| Dimethylsulfoxide | 25 | 71.3 | 17.3 | 19.2 |
| | 60 | 73.8 | 16.6 | 18.7 |
| | 100 | 77.2 | 15.9 | 18.4 |
| Ethanol | 25 | 58.7 | 16.0 | 21.9 |
| Ethyl acetate | 25 | 98.5 | 15.5 | 9.2 |
| | 60 | 103.3 | 14.8 | 8.8 |
| | 100 | 103.3 | 14.8 | 8.8 |
| Ethyl butyl ketone | 25 | 139.8 | 16.1 | 7.4 |
| | 60 | 146.0 | 15.3 | 7.5 |
| | 100 | 146.0 | 15.3 | 7.5 |
| Ethylene chlorohydrin | 25 | 66.9 | 16.5 | 19.1 |
| | 60 | 68.6 | 15.9 | 19.0 |
| | 100 | 77.9 | 15.1 | 17.3 |

TABLE 9 (continued)
Molar Volumes, Nonpolar Cohesion Parameters and Polar Cohesion
Parameters of Polar Liquids at Various Temperatures

| Liquid | $t/^{\circ}\text{C}$ | $V/\text{cm}^3\text{mol}^{-1}$ | Nonpolar, $\delta_d/\text{MPa}^{1/2}$ | Polar, $\delta_p/\text{MPa}^{1/2}$ |
|---------------------------------|----------------------|--------------------------------|--|---------------------------------------|
| Ethylenediamine | 0 | 65.6 | 17.1 | 19.9 |
| | 25 | 67.3 | 16.6 | 19.1 |
| | 45 | 68.7 | 16.2 | 18.4 |
| | 60 | 69.7 | 15.9 | 18.1 |
| | 100 | 72.9 | 15.2 | 17.4 |
| Ethylene glycol | 25 | 56.0 | 17.3 | 31.3 |
| Furfural | 0 | 81.4 | 19.3 | 16.1 |
| | 25 | 83.2 | 18.7 | 15.4 |
| | 45 | 84.8 | 18.2 | 14.9 |
| | 60 | 86.9 | 17.9 | 15.0 |
| | 100 | 89.4 | 16.9 | 14.4 |
| Methyl Cellosolve® | 25 | 79.4 | 16.1 | 15.7 |
| | 60 | 82.3 | 15.5 | 15.3 |
| | 100 | 86.0 | 14.8 | 16.1 |
| Methyl ethyl ketone, 2-butanone | 0 | 87.3 | 16.3 | 11.4 |
| | 25 | 90.1 | 15.8 | 11.0 |
| | 45 | 92.6 | 15.1 | 10.5 |
| | 60 | 94.5 | 15.0 | 10.6 |
| | 100 | 100.0 | 14.2 | 10.0 |
| <i>N</i> -Methyl-2-pyrrolidone | 0 | 94.5 | 19.2 | — |
| | 25 | 96.6 | 18.5 | — |
| | 45 | 98.6 | 17.9 | 7.6 |
| | 60 | 99.6 | 17.8 | 13.0 |
| | 100 | 103.3 | 16.9 | 12.3 |
| Nitrobenzene | 25 | 102.7 | 20.1 | 9.5 |
| | 60 | 105.5 | 19.3 | 8.7 |
| | 100 | 109.1 | 18.2 | 9.1 |
| Nitromethane | 0 | 53.1 | 17.3 | 20.7 |
| | 25 | 54.3 | 16.8 | 20.0 |
| | 45 | 55.3 | 16.4 | 19.4 |
| | 60 | 56.3 | 16.1 | 18.4 |
| | 100 | 59.3 | 15.4 | 16.8 |
| Acetylacetone, pentanedione | 25 | 103.1 | 17.5 | 10.8 |
| 1-Pentanol, amyl alcohol | 25 | 108.7 | 16.1 | 14.7 |
| Phenol | 25 | 89.3 | 20.2 | 13.0 |
| | 100 | 95.2 | 18.2 | 13.9 |
| 1-Propanol | 25 | 75.2 | 15.9 | 18.9 |
| 2-Propanol, isopropanol | 25 | 77.0 | 15.6 | 19.0 |
| Propionitrile | 0 | 68.7 | 16.9 | 15.1 |
| | 25 | 70.9 | 16.3 | 14.7 |
| | 45 | 72.9 | 15.9 | 14.4 |
| | 60 | 74.4 | 15.6 | 14.1 |
| | 100 | 79.0 | 14.8 | 13.7 |
| Pyridine | 0 | 78.7 | 20.8 | 9.3 |
| | 25 | 80.9 | 20.2 | 7.9 |
| | 45 | 82.9 | 19.6 | 6.5 |
| | 60 | 83.9 | 19.2 | 6.2 |
| | 100 | 87.4 | 18.1 | 6.6 |
| 2-Pyrrolidone | 25 | 76.5 | 20.1 | 14.1 |
| | 45 | 77.4 | 20.2 | 13.3 |
| Tetrahydrofuran | 0 | 79.3 | 17.7 | 8.1 |
| | 25 | 81.8 | 17.1 | 7.4 |

Adapted from Helpinstill, J. G. and Van Winkle, M., *Ind. Eng. Chem. Proc. Des. Dev.*, 7, 213, 1968.

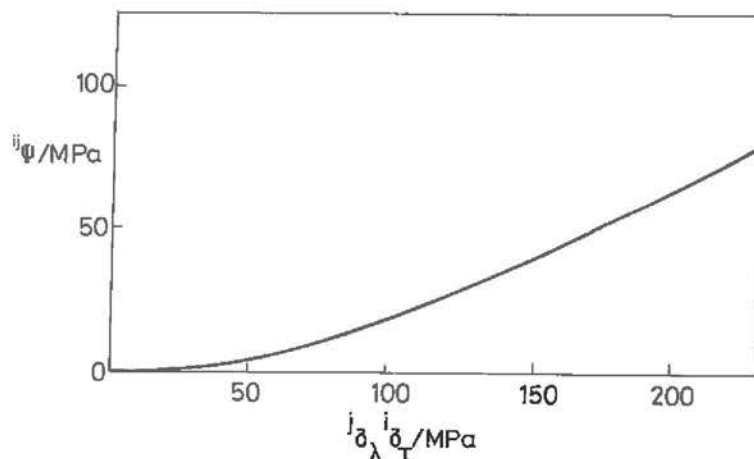


FIGURE 4. Contribution of induction interactions to interchange cohesive pressure at 25°C. (Adapted from Blanks, R. F. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 3, 1, 1964.)

TABLE 10
Values of Induction Cohesive Pressure Correction Factor (ψb)

| Component <i>i</i> (interacting with liquid <i>j</i>) | ψb | Ref. |
|---|----------|------|
| Induction-free system | 1.00 | — |
| Alkane | 0.21 | 113 |
| Alkane | 0.20 | 115 |
| Alkene | 0.17 | 113 |
| Alkene | 0.55 | 115 |
| Aromatic | 0.10 | 113 |
| Aromatic | 0.05 | 115 |
| Vapor of \dot{r} | 0.63 | 120 |
| Vulcanized polyisoprene (natural rubber) | 0.19 | 118 |
| Polymers, surfactants, pigments ^b | 0.25 | 9 |

^a From surface free energy, Equation 17, Chapter 17.

^b Based on Equation 55, and Equation 25, Chapter 17 (the validity of which have been questioned).

Adapted from Hansen, C. M. and Beerbower, A., *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Standen, A., Ed., Interscience, New York, 1971, 889. (Related data appear in Table 13.)

Further development of these ideas led to the MOSCED (*modified separation of cohesive energy density*) method (Sections 5.13 and 7.8).

For the special case of a solute in a supercritical solvent (Sections 11.3 and 12.2), Kramer and Thomas¹⁵⁷ neglected the polar and hydrogen-bonding contributions to the cohesive properties of the solvent in its supercritical state while retaining these contributions for the solute and introducing a binary interaction parameter $\psi\beta$ for solute-solvent interactions so Equation 52b simplified to

$${}^iA = ({}^i\delta_d - {}^j\delta_d)^2 + {}^j\delta_r^2 - \psi\beta \quad (52c)$$

Seidel and Bittrich¹¹⁶ from a theoretical model evaluated polar contributions to the enthalpy of vaporization, giving totals which for liquids without hydrogen bonding were in good agreement with experiment.

5.9 HANSEN PARAMETERS

Hansen⁹⁻³⁰ proposed a practical extension of the Hildebrand parameter method to polar and hydrogen-bonding systems, primarily for use in polymer-liquid interactions (Section 14.5). It was assumed that dispersion, polar, and hydrogen-bonding parameters were valid simultaneously, related by Equation 54, with the values of each component being determined empirically on the basis of many experimental observations:

$$\delta_i^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (54)$$

These parameters are listed in Table 11. Hansen's total cohesion parameter, δ_i , should equal the Hildebrand parameter, although the two quantities may differ for materials with specific interactions when they are determined by different methods. The three component parameters were plotted on a set of three mutually perpendicular axes.

For liquids, the dispersion component, δ_d , obtained by homomorph methods (Section 6.7) was subtracted from the total cohesive property, and the remainder was split into hydrogen-bonding and polar contributions so as to optimize the description of the miscibility behavior of all the polymer-liquid systems investigated (comprising several polymers and many liquids). Both empirical relations (Section 8.2) such as Böttcher's equation¹¹⁷ and group methods (Section 6.8) were used. Once the three component parameters for each liquid were evaluated, the set of parameters for each polymer could be determined. Burrell⁵⁰ pointed out that methods such as this tend to distort the relative magnitudes of the various intermolecular effects, the polar contribution to the cohesive pressure usually being very small in relation to that of hydrogen bonding in those situations where hydrogen bonds exist.

Other Hansen parameter values are presented in Table 12. These data, which draw on earlier results of Hansen,^{10,11} as well as on other calculations and observations of elastomer swelling, are based on compilations by Beerbower and Dickey¹¹⁸ and by Gardon and Teas.¹¹⁹ Their inclusion is warranted because they provide information on a wide range of pure and mixed liquids. In addition, Table 18 (Section 5.11) presents Hansen parameters for an even wider range of liquids, calculated by the semi-empirical methods described in Sections 5.11 and 7.2.

Occasional negative values of the component parameters have been attributed to the center of maximum interaction lying closer to the axis than the radius of the solubility sphere (see below). The scale on the dispersion axis was doubled with the aim of providing approximately spherical "volumes" of solubility which were drawn up for each solute and then compared with the point locations in this space for each liquid (Figure 5). The distance of the liquid coordinates (${}^i\delta_d$, ${}^i\delta_p$, ${}^i\delta_h$) from the center point (${}^j\delta_d$, ${}^j\delta_p$, ${}^j\delta_h$) of the solute sphere of solubility is

$${}^iR = [4({}^i\delta_d - {}^j\delta_d)^2 + ({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2]^{1/2} \quad (55)$$

This may be expressed in a form similar to that of Equation 52b, with $b = 0.25$ and $\delta_i^2 = \delta_p^2 + \delta_h^2$:

$${}^iA = ({}^i\delta_d - {}^j\delta_d)^2 + 0.25 [({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2] \quad (56)$$

The distance iR in Equation 55 can be compared with the radius jR of a solute sphere of solubility, and if ${}^iR < {}^jR$ there is a high likelihood of the liquid i dissolving j . This was

TABLE 11
Hansen and Beerbower's 1971 Parameters for Liquids at 25°C

| Liquid | $V/\text{cm}^3 \text{ mol}^{-1}$ | δ_d | δ_p | δ_h | δ_t |
|------------------------------------|----------------------------------|-------------------|------------------|------------------|------------|
| Alkanes | | | | | |
| Butane | 101.4 | 14.1 | 0.0 | 0.0 | 14.1 |
| Pentane | 116.2 | 14.5 | 0.0 | 0.0 | 14.5 |
| Isopentane, 2-methylbutane | 117.4 | 13.7 | 0.0 | 0.0 | 13.7 |
| Hexane | 131.6 | 14.9 | 0.0 | 0.0 | 14.9 |
| Heptane | 147.4 | 15.3 | 0.0 | 0.0 | 15.3 |
| Octane | 163.5 | 15.5 | 0.0 | 0.0 | 15.5 |
| 2,2,4-Trimethylpentane, isooctane | 166.1 | 14.3 | 0.0 | 0.0 | 14.3 |
| Nonane | 179.7 | 15.8 | 0.0 | 0.0 | 15.8 |
| Decane | 195.9 | 15.8 | 0.0 | 0.0 | 15.8 |
| Dodecane | 228.6 | 16.0 | 0.0 | 0.0 | 16.0 |
| Hexadecane | 294.1 | 16.4 | 0.0 | 0.0 | 16.4 |
| Eicosane | 359.8 | 16.6 | 0.0 | 0.0 | 16.6 |
| Cyclohexane | 108.7 | 16.8 | 0.0 | 0.2 ^a | 16.8 |
| Methylcyclohexane | 128.3 | 16.0 | 0.0 | 1.0 | 16.0 |
| cis-Decahydronaphthalene, decalin | 156.9 | 18.8 | 0.0 | 0.0 | 18.8 |
| trans-Decahydronaphthalene | 159.9 | 18.0 | 0.0 | 0.0 | 18.0 |
| Aromatic Hydrocarbons | | | | | |
| Benzene | 89.4 | 18.4 | 0.0 ^a | 2.0 | 18.6 |
| Toluene, methylbenzene | 106.8 | 18.0 | 1.4 | 2.0 | 18.2 |
| Naphthalene ^b | 111.5 | 19.2 | 2.0 | 3.9 ^a | 20.3 |
| Styrene, ethenylbenzene | 115.6 | 18.6 | 1.0 | 4.1 | 19.0 |
| o-Xylene, 1,2-dimethylbenzene | 121.2 | 17.8 | 1.0 | 3.1 | 18.0 |
| Ethylbenzene | 123.1 | 17.8 | 0.6 | 1.4 | 17.8 |
| 1-Methylnaphthalene | 138.8 | 20.7 | 0.8 | 4.7 | 21.2 |
| Mesitylene, 1,3,5-trimethylbenzene | 139.8 | 18.0 | 0.0 | 0.6 | 18.0 |
| Tetrahydronaphthalene, tetralin | 136.0 ^a | 19.6 ^a | 2.0 | 2.9 | 20.0 |
| Diphenyl | 154.1 | 21.5 | 1.0 | 2.1 | 21.6 |
| 1,4-Diethylbenzene | 156.9 | 18.0 | 0.0 | 0.6 | 18.0 |

| | | | | |
|---------------------------------|-------------------|-----|-----|------|
| Tetrahydronaphthalene, tetralin | 18.0 | 0.0 | 0.6 | 18.0 |
| Diphenyl | 19.6 ^d | 2.0 | 2.9 | 20.0 |
| 1,4-Diethylbenzene | 21.5 | 1.0 | 2.1 | 21.6 |
| | 156.9 | 0.0 | 0.6 | 18.0 |

Halohydrocarbons

| | | | | |
|---|--------------------|------------------|------------------|-------------------|
| Chloromethane, methyl chloride | 55.4 | 6.1 | 3.9 | 17.0 |
| Dichloromethane, methylene dichloride | 63.9 | 6.3 | 6.1 | 20.3 |
| Bromochloromethane | 65.0 | 5.7 | 3.5 | 18.6 |
| Chlorodifluoromethane, Freon 22 | 72.9 | 6.3 | 5.7 | 14.9 |
| Dichlorofluoromethane, Freon 21 | 75.4 | 3.1 | 5.7 | 17.1 |
| Bromoethane, ethyl bromide | 76.9 | 3.1 | 5.7 | 17.0 |
| 1,1-Dichloroethylene | 79.0 | 6.8 | 4.5 | 18.8 |
| 1,2-Dichloroethane, ethylene dichloride | 79.4 | 7.4 | 4.1 | 20.9 |
| Diiodomethane, methylene diiodide | 80.5 | 3.9 | 5.5 | 19.0 |
| Trichloromethane, chloroform | 80.7 | 3.1 | 5.7 | 19.0 |
| 1,1-Dichloroethane, ethylidene chloride | 84.8 | 8.2 | 0.4 | 18.5 |
| 1,1-Dibromoethane, ethylidene bromide | — | 5.1 ^f | 6.5 ^t | 20.2 ^f |
| 1,2-Dibromoethane, ethylene dibromide | 87.0 | 6.8 | 12.1 | 23.9 |
| Tribromomethane, bromoform | 87.5 | 4.1 | 6.1 | 22.7 ^e |
| 1-Chloropropane, propyl chloride | 88.1 | 7.8 | 2.0 | 17.8 |
| Trichloroethylene | 90.2 | 3.1 | 5.3 | 19.0 |
| Dichlorodifluoromethane, Freon 12 | 92.3 | 2.0 | 0.0 | 12.5 |
| Trichlorofluoromethane, Freon 11 | 92.8 | 2.1 | 0.0 | 15.4 |
| Bromotrifluoromethane | 97.0 | 2.5 | 0.0 | 9.9 |
| Tetrachloromethane, carbon tetrachloride | 97.1 | 0.0 | 0.6 | 17.8 |
| 1,1,1-Trichloroethane | 100.4 | 4.3 | 2.1 | 17.7 |
| Tetrachloroethylene, perchloroethylene | 101.1 | 6.5 | 2.9 ^a | 20.3 |
| Chlorobenzene | 102.1 | 4.3 | 2.0 | 19.6 |
| Butyl chloride, 1-chlorobutane | 104.9 | 16.4 | 2.1 | 17.4 |
| 1,1,2,2-Tetrachloroethane | 105.2 ^a | 5.5 | 2.1 | 21.6 |
| Bromobenzene | 105.3 | 5.1 | 9.4 | 17.4 |
| <i>o</i> -Dichlorobenzene | 112.8 | 5.5 | 4.1 | 21.7 |
| Benzyl chloride | 115.0 | 6.3 | 3.3 | 20.5 |
| 1,1,2,2-Tetrabromoethane ^e | 116.8 | 7.2 | 2.7 | 20.3 |
| 1,2-Dichlorotetrafluoroethane, Freon 114 ^c | 117.0 | 5.1 | 8.2 | 24.7 |
| 1,1,2-Trichlorotrifluoroethane, Freon 113 | 119.2 | 1.8 | 0.0 | 12.8 |
| Cyclohexyl chloride | 119.2 | 1.6 | 0.0 | 14.7 |
| 1-Bromonaphthalene | 121.3 | 17.4 | 2.1 | 18.4 |
| Trichlorobiphenyl ^e | 140.0 | 3.1 | 4.1 | 20.9 |
| Perfluor(methylcyclohexane) | 187.0 | 19.2 | 4.1 | 20.3 |
| Perfluor(dimethylcyclohexane ^d) | 196.0 | 0.0 | 0.0 | 12.5 |
| Perfluorheptane | 217.4 | 0.0 | 0.0 | 12.5 |
| | 227.3 | 0.0 | 0.0 | 12.1 |

TABLE 11 (continued)
Hansen and Beerbower's 1971 Parameters for Liquids at 25°C

| Liquid | $V/\text{cm}^3 \text{ mol}^{-1}$ | δ_d | δ_p | $\delta/M\text{Pa}^{1/2}$ | δ_b | δ_t |
|---|----------------------------------|-------------------|------------|---------------------------|------------|-------------------|
| Ethers | | | | | | |
| Furan | 72.5 | 17.8 | 1.8 | | 5.3 | 18.6 |
| Epichlorohydrin | 79.9 | 19.0 | 10.2 | | 3.7 | 21.9 |
| Tetrahydrofuran | 81.7 | 16.8 | 5.7 | | 8.0 | 19.4 |
| 1,4-Dioxane | 85.7 | 19.0 | 1.8 | | 7.4 | 20.5 |
| Dimethoxymethane, methylal ^c | 88.8 | 15.1 | 1.8 | | 8.6 | 17.5 |
| Diethyl ether | 104.8 | 14.5 | 2.9 | | 5.1 | 15.8 |
| Bis(2-chloroethyl) ether | 117.6 | 18.8 | 9.0 | | 5.7 | 21.6 ^a |
| Anisole, methoxybenzene ^c | 119.1 | 17.8 | 4.1 | | 6.8 | 19.5 |
| Di-(2-methoxyethyl) ether | 142.0 | 15.8 | 6.1 | | 9.2 | 19.3 |
| Dibenzyl ether ^c | 192.7 | 17.4 | 3.7 | | 7.4 | 19.3 |
| Di-(2-chloroisopropyl) ether ^c | 146.0 | 19.0 | 8.2 | | 5.1 | 21.3 |
| Bis-(<i>m</i> -phenoxyphenol) ether | 373.0 | 19.6 | 3.1 | | 5.1 | 20.5 |
| Ketones | | | | | | |
| Acetone, 2-propanone | 74.0 | 15.5 | 10.4 | | 7.0 | 20.0 |
| Methyl ethyl ketone, 2-butanone | 90.1 | 16.0 | 9.0 | | 5.1 | 19.0 |
| Cyclohexanone | 104.0 | 17.8 | 6.3 | | 5.1 | 19.6 |
| Diethyl ketone | 106.4 | 15.8 | 7.6 | | 4.7 | 18.1 |
| Mesityl oxide | 115.6 | 16.4 | 6.1 | | 6.1 | 18.9 |
| Acetophenone | 117.4 | 19.6 ^a | 8.6 | | 3.7 | 21.8 |
| Methyl isobutyl ketone | 125.8 | 15.3 | 6.1 | | 4.1 | 17.0 |
| Methyl isomyl ketone | 142.8 | 16.0 | 5.7 | | 4.1 | 17.4 |
| Isophorone | 150.5 | 16.6 | 8.2 | | 7.4 | 19.9 |
| Diisobutyl ketone | 177.1 | 16.0 | 3.7 | | 4.1 | 16.9 |

Aldehydes

| | | | | | |
|---------------------------------|-------|-------------------|------------------|------------------|------|
| Acetaldehyde ^c | 57.1 | 14.7 | 8.0 | 11.3 | 20.2 |
| Furfural, 2-furancarboxaldehyde | 83.2 | 18.6 ^a | 14.9 | 5.1 | 24.4 |
| Butyraldehyde, butanal | 88.5 | 14.7 | 5.3 ^a | 7.0 ^a | 17.1 |
| Benzaldehyde | 101.5 | 19.4 | 7.4 | 5.3 | 21.5 |

Esters

| | | | | | |
|--|-------|-------------------|-------------------|------------------|------|
| Ethylene carbonate | 66.0 | 19.4 | 21.7 | 5.1 | 29.6 |
| γ -Butyrolactone | 76.8 | 19.0 | 16.6 | 7.4 | 26.3 |
| Methyl acetate | 79.7 | 15.5 | 7.2 | 7.6 | 18.7 |
| Ethyl formate | 80.2 | 15.5 | 7.2 | 7.6 | 18.7 |
| Propylene-1,2-carbonate | 85.0 | 20.0 | 18.0 | 4.1 | 27.3 |
| Ethyl chloroformate | 95.6 | 15.6 | 10.0 | 6.8 | 19.7 |
| Ethyl acetate | 98.5 | 15.8 ^a | 5.3 | 7.2 ^a | 18.1 |
| Trimethyl phosphate | 99.9 | 16.8 | 16.0 | 10.2 | 25.3 |
| Diethyl carbonate | 121 | 16.6 | 3.1 | 6.1 | 17.9 |
| Diethyl sulfate | 131.5 | 15.8 | 14.7 | 7.2 | 22.8 |
| Butyl acetate | 132.5 | 15.8 | 3.7 | 6.3 | 17.4 |
| Isobutyl acetate | 133.5 | 15.1 | 3.7 | 6.3 | 16.8 |
| 2-Ethoxyethyl acetate, Cellosolve [®] acetate | 136.2 | 16.0 | 4.7 | 10.6 | 20.0 |
| Isomyl acetate | 148.8 | 15.3 | 3.1 | 7.0 | 17.1 |
| Isobutyl isobutyrate | 163 | 15.1 | 2.9 | 5.9 | 16.5 |
| Dimethyl phthalate | 163 | 18.6 ^a | 10.8 ^a | 4.9 | 22.1 |
| Ethyl cinnamate | 166.8 | 18.4 | 8.2 | 4.1 | 20.6 |
| Triethyl phosphate | 171.0 | 16.8 | 11.5 | 9.2 | 22.3 |
| Diethyl phthalate | 198 | 17.6 | 9.6 | 4.5 | 20.6 |
| Dibutyl phthalate | 266 | 17.8 ^a | 8.6 | 4.1 | 20.2 |
| Butyl benzyl phthalate | 306 | 19.0 | 11.3 | 3.1 | 22.3 |
| Tricresyl phosphate | 316 | 19.0 | 12.3 | 4.5 | 23.1 |
| Tributyl phosphate | 345 | 16.4 | 6.3 | 4.3 | 18.1 |
| Isopropyl palmitate ^c | 330 | 14.3 | 3.9 | 3.7 | 15.3 |
| Dibutyl sebacate | 339 | 13.9 | 4.5 | 4.1 | 15.2 |
| Methyl oleate ^d | 340 | 14.5 | 3.9 | 3.7 | 15.5 |
| Dioctyl phthalate | 377 | 16.6 | 7.0 | 3.1 | 18.2 |
| Dibutyl stearate ^c | 382 | 14.5 | 3.7 | 3.5 | 15.4 |

TABLE 11 (continued)
Hansen and Beerbower's 1971 Parameters for Liquids at 25°C

| Liquid | V/cm ³ mol ⁻¹ | δ/MPa ^{1/2} | | | |
|---------------------------------------|-------------------------------------|----------------------|------------------|------------------|------|
| | | δ _a | δ _b | δ _t | |
| Nitrogen Compounds | | | | | |
| Acetonitrile | 52.6 | 15.3 | 18.0 | 6.1 | 24.4 |
| Acrylonitrile, 2-propenenitrile | 67.1 | 16.4 | 17.4 | 6.8 | 24.8 |
| Propionitrile | 70.9 | 15.3 | 14.3 | 5.5 | 21.7 |
| Butyronitrile | 87.0 | 15.3 | 12.5 | 5.1 | 20.4 |
| Benzonitrile | 102.6 | 17.4 | 9.0 | 3.3 | 19.9 |
| Nitroethane | 54.3 | 15.8 | 18.8 | 5.1 | 25.1 |
| 2-Nitropropane | 71.5 | 16.0 | 15.5 | 4.5 | 22.7 |
| Nitrobenzene | 86.9 | 16.2 | 12.1 | 4.1 | 20.6 |
| Ethanolamine, 2-aminoethanol | 102.7 | 20.0 | 8.6 | 4.1 | 22.2 |
| Ethylenediamine | 60.2 | 17.2 | 15.6 | 21.3 | 31.5 |
| 1,1-Dimethylhydrazine ^c | 67.3 | 16.6 | 8.8 | 17.0 | 25.3 |
| 2-Pyrrolidone | 76.0 | 15.3 | 5.9 | 11.0 | 19.8 |
| Pyridine | 76.4 | 19.4 | 17.4 | 11.3 | 28.4 |
| Propylamine | 80.9 | 19.0 | 8.8 | 5.9 | 21.8 |
| Morpholine | 83.0 | 17.0 | 4.9 | 8.6 | 19.7 |
| Aniline | 87.1 | 18.8 | 4.9 | 9.2 | 21.5 |
| N-Methyl-2-pyrrolidone | 91.5 | 19.4 | 5.1 | 10.2 | 22.6 |
| Butylamine, 1-butanamine | 96.5 | 18.0 | 12.3 | 7.2 | 22.9 |
| Diethylamine | 99.0 | 16.2 ^a | 4.5 ^b | 8.0 ^b | 18.6 |
| Diethylenetriamine | 103.2 | 14.9 | 2.3 | 6.1 | 16.3 |
| Cyclohexylamine | 108.0 | 16.8 | 13.3 | 14.3 | 25.8 |
| Quinoline | 115.2 | 17.4 | 3.1 | 6.6 | 18.9 |
| Dipropylamine | 118.0 | 19.4 | 7.0 | 7.6 | 22.0 |
| Formamide | 136.9 | 15.3 | 1.4 | 4.1 | 15.9 |
| N,N-Dimethylformamide | 39.8 | 17.2 | 26.2 | 19.0 | 36.6 |
| N,N-Dimethylacetamide | 77.0 | 17.4 | 13.7 | 11.3 | 24.8 |
| Tetramethylurea | 92.5 | 16.8 | 11.5 | 10.2 | 22.7 |
| Hexamethyl phosphoramide ^c | 120.4 | 16.8 | 8.2 | 11.1 | 21.7 |
| | 175.7 | 23.2 | 8.6 | 11.3 | 23.2 |

120.4
175.716.8
23.2Hexamethyl phosphoramide^c8.2
8.611.1
11.321.7
23.2

Sulfur Compounds

| | | | | | |
|--|-------|------|------|------|------|
| Carbon disulfide | 60.0 | 20.5 | 0.0 | 0.6 | 20.5 |
| Dimethylsulfoxide | 71.3 | 18.4 | 16.4 | 10.2 | 26.7 |
| Ethanesithiol ^a , ethyl mercaptan | 74.3 | 15.8 | 6.6 | 7.2 | 18.6 |
| Dimethyl sulfone ^b | 75 | 19.0 | 19.4 | 12.3 | 29.8 |
| Diethyl sulfide | 108.2 | 17.0 | 3.1 | 2.1 | 17.4 |

Acid Halides and Anhydrides

| | | | | | |
|---------------------------------|------|-------------------|-------------------|-------------------|------|
| Acetyl chloride | 71.0 | 15.8 | 10.6 | 3.9 | 19.4 |
| Succinic anhydride ^b | 66.8 | 18.6 | 19.2 | 16.6 | 31.5 |
| Acetic anhydride | 94.5 | 16.0 ^c | 11.7 ^a | 10.2 ^a | 22.3 |

Alcohols

| | | | | | |
|--|-------|------|------|------|------|
| Methanol | 40.7 | 15.1 | 12.3 | 22.3 | 29.6 |
| Ethanol | 58.5 | 15.8 | 8.8 | 19.4 | 26.5 |
| Ethylene cyanohydrin, hydracrylonitrile | 68.3 | 17.2 | 18.8 | 17.6 | 31.0 |
| Allyl alcohol, 2-propen-1-ol ^c | 68.4 | 16.2 | 10.8 | 16.8 | 25.7 |
| 1-Propanol | 75.2 | 16.0 | 6.8 | 17.4 | 24.5 |
| 2-Propanol | 76.8 | 15.8 | 6.1 | 16.4 | 23.5 |
| 3-Chloropropanol | 84.2 | 17.6 | 5.7 | 14.7 | 23.6 |
| Furfuryl alcohol | 86.5 | 17.4 | 7.6 | 15.1 | 24.3 |
| 1-Butanol | 91.5 | 16.0 | 5.7 | 15.8 | 23.1 |
| 2-Butanol | 92.0 | 15.8 | 5.7 | 14.5 | 22.2 |
| Isobutanol, 2-methyl-1-propanol | 92.8 | 15.1 | 5.7 | 16.0 | 22.7 |
| Benzyl alcohol, benzenemethanol | 103.6 | 18.4 | 6.3 | 13.7 | 23.8 |
| Cyclohexanol | 106.0 | 17.4 | 4.1 | 13.5 | 22.4 |
| 1-Pentanol, amyl alcohol | 109.0 | 16.0 | 4.5 | 13.9 | 21.7 |
| 2-Ethyl-1-butanol | 123.2 | 15.8 | 4.3 | 13.5 | 21.2 |
| Diacetone alcohol | 124.2 | 15.8 | 8.2 | 10.8 | 20.8 |
| 1,3-Dimethyl-1-butanol | 127.2 | 15.3 | 3.3 | 12.3 | 19.9 |
| Ethyl lactate | 115 | 16.0 | 7.6 | 12.5 | 21.6 |
| Butyl lactate | 149 | 15.8 | 6.5 | 10.2 | 19.9 |
| Ethylene glycol monomethyl ether, methyl Cellosolve ^b | 79.1 | 16.2 | 9.2 | 16.4 | 24.8 |

TABLE 11 (continued)
Hansen and Beerbower's 1971 Parameters for Liquids at 25°C

| Liquid | V/cm ³ mol ⁻¹ | $\delta/\text{MPa}^{1/2}$ | | | |
|--|-------------------------------------|---------------------------|-----------------------|------------|-------------------------|
| | | δ_d | δ_p | δ_h | δ_t |
| Ethylene glycol monoethyl ether, Cellosolve® | 97.8 | 16.2 | 9.2 | 14.3 | 23.5 |
| Diethylene glycol monomethyl ether, methyl Carbitol® | 118.0 | 16.2 | 7.8 | 12.7 | 22.0 |
| Diethylene glycol monoethyl ether, Carbitol® | 130.9 | 16.2 | 9.2 | 12.3 | 22.3 |
| Ethylene glycol monobutyl ether, butyl Cellosolve® | 131.6 | 16.0 | 5.1 | 12.3 | 20.8 |
| 2-Ethyl-1-hexanol | 157.0 | 16.0 | 3.3 | 11.9 | 20.2 |
| 1-Octanol | 157.7 | 17.0 | 3.3 | 11.9 | 21.0 |
| 2-Octanol | 159.1 | 16.2 | 4.9 | 11.1 | 20.2 |
| Diethylene glycol monobutyl ether, butyl Carbitol® | 170.6 | 16.0 | 7.0 | 10.6 | 20.4 |
| 1-Decanol | 191.8 | 17.6 | 2.7 | 10.0 | 20.4 |
| Tridecyl alcohol, 1-tridecanol ^d | 242 | 14.3 | 3.1 | 9.0 | 17.2 |
| 'Nonyl' phenoxy ethanol ^f | 275 | 16.8 | 10.2 | 8.4 | 21.4 |
| Oleyl alcohol, 9-octadecen-1-ol ^d | 316 | 14.3 | 2.7 | 8.0 | 16.6 |
| Triethylene glycol mono-oleyl ether | 418.5 | 13.3 | 3.1 | 8.4 | 16.0 |
| Acids | | | | | |
| Formic acid, methanoic acid | 37.8 | 14.3 | 11.9 | 16.6 | 24.9 |
| Acetic acid, ethanoic acid | 57.1 | 14.5 | 8.0 | 13.5 | 21.4 |
| Benzoic acid ^b | 100 | 18.2, 21.5 ^f | 7.0, 5.7 ^f | 9.8 | 21.8, 24.3 ^f |
| Butyric acid, 1-butanoic acid ^c | 110 | 14.9 | 4.1 | 10.6 | 18.8 |
| Octanoic acid ^f | 159 | 15.1 | 3.3 | 8.2 | 17.5 |
| Oleic acid, 9-octadecenoic acid ^b | 320 | 14.3 | 3.1 | 5.5 | 15.6 |
| Stearic acid, octadecanoic acid ^b | 326 | 16.4 | 3.3 | 5.5 | 17.6 |
| Phenols | | | | | |
| Phenol | 87.5 | 18.0 | 5.9 | 14.9 | 24.1 |
| 1,3-Benzenediol, resorcinol ^b | 87.5 | 18.0 | 8.4 | 21.1 | 29.0 |

| | | | | | |
|---|-------|-------------------|-------------------|-------------------|------|
| 1,3-Benzenediol, resorcinol ^b | 87.5 | 18.0 | 5.9 | 14.9 | 24.1 |
| | 87.5 | 18.0 | 8.4 | 21.1 | 29.0 |
| <i>m</i> -Cresol, 3-methylphenol | 104.7 | 18.0 | 5.1 | 12.9 | 22.7 |
| <i>o</i> -Methoxyphenol ^c | 109.5 | 18.0 | 8.2 | 13.3 | 23.8 |
| Methyl salicylate | 129 | 16.0 | 8.0 | 12.3 | 21.7 |
| 'Nonyl' phenol ^d | 231 | 16.6 | 4.1 | 9.2 | 19.4 |
| Water ^e | 18.0 | 15.6 ^f | 16.0 ^g | 42.3 ^h | 47.8 |
| Polyhydric Alcohols | | | | | |
| Ethylene glycol, 1,2-ethanediol | 55.8 | 17.0 | 11.0 | 26.0 | 32.9 |
| Glycerol, 1,2,3-propanetriol | 73.3 | 17.4 | 12.1 | 29.3 | 36.1 |
| Propylene glycol, propanediol | 73.6 | 16.8 | 9.4 | 23.3 | 30.2 |
| 1,3-Butanediol | 89.9 | 16.6 | 10.0 | 21.5 | 28.9 |
| Diethylene glycol | 95.3 | 16.2 | 14.7 | 20.5 | 29.9 |
| Triethylene glycol | 114.0 | 16.0 | 12.5 | 18.6 | 27.5 |
| Hexylene glycol | 123.0 | 15.8 | 8.4 | 17.8 | 25.2 |
| Dipropylene glycol ⁱ (mixed isomers) | 131.3 | 16.0 | 20.3 | 18.4 | 31.7 |

^a Altered from previously published 1967 value; additional values based on 1967 data appear in Table 12.

^b Solid, treated as subcooled liquid.

^c Values uncertain.

^d Impure commercial product of this nominal formula.

^e Subsequently recalculated by Wu, P. L., Beerbower, A., and Martin, A., *J. Pharm. Sci.*, 71, 1285, 1982.

^f Subsequently recalculated in 1974 as reported by Beerbower, A., Wu, P. L., and Martin, A., *J. Pharm. Sci.*, 73, 179, 1984.

Adapted from Hansen, C. M. and Beerbower, A., *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Standen, A., Ed., Interscience, New York, 1971, Suppl. Vol., 889.

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TABLE 12
Hansen Parameters for Liquids, Refrigerants, and Liquid Mixtures at 25°C, Based
on 1967 Data

| Liquids | $\delta/\text{MPa}^{1/2}$ | | |
|---|---------------------------|-------------------------|-------------------------|
| | δ_d | δ_p | δ_h |
| Acetic acid, ethanoic acid | 14.5 | 8.0 | 13.5 |
| Acetone, 2-propanone | 15.6 | 12.3, 10.4 ^a | 7.0 |
| Acetonitrile | 15.3 | 18.0 | 6.1 |
| Acetophenone | 17.6 ^a | 8.6 ^a | 3.7 ^a |
| Acetyl chloride | 15.8 ^a | 10.6 ^a | 3.9 ^a |
| Acrylonitrile, 2-propenenitrile | 16.4 | 17.4 | 6.8 |
| Aniline, benzeneamine | 19.4, 20.1 ^a | 5.1, 7.4 ^a | 10.2, 12.3 ^a |
| Benzaldehyde | 19.4 | 7.4 | 5.3 |
| Benzene | 18.4 | 1.0 | 2.1 |
| Benzoic acid | 18.2 | 7.0 | 9.8 |
| Benzonitrile | 17.4 ^a | 13.3 ^a | 5.1 ^a |
| Benzyl alcohol, benzenemethanol | 18.4 | 6.3 | 13.7 |
| Benzyl chloride, (chloromethyl)benzene | 17.6, 18.8 ^a | 7.2 | 2.7 |
| Biphenyl | 21.1 ^a | 1.0 ^a | 2.0 ^a |
| Bromobenzene | 19.0 | 5.5 | 2.1 |
| Bromoethane | 16.6 ^a | 8.0 ^a | 5.1 ^a |
| 1-Bromonaphthalene | 20.3 ^a | 3.1 ^a | 4.1 ^a |
| Butane | 13.7, 14.1 ^a | 0.0 | 0.0 |
| 1,3-Butanediol | 16.6 ^a | 10.0 ^a | 21.5 ^a |
| 1-Butanol | 16.0 | 5.7 | 15.8 |
| 2-Butanol | 15.8 | 5.7 | 14.5 |
| Butyl acetate | 15.8 | 3.7 | 6.3 |
| Butylamine, 1-butanamine | 15.6 | 3.7 | 7.2 |
| Butyl Carbitol [®] , 2-(2-butoxyethoxy)ethanol | 16.0, 16.4 ^a | 7.0 | 10.6 |
| Butyl Cellosolve [®] , 2-butoxyethanol | 16.0 | 5.1, 6.3 ^a | 12.3, 12.1 ^a |
| Butyl chloride, 1-chlorobutane | 16.2 ^a | 5.5 ^a | 2.0 ^a |
| Butyl lactate | 15.5 ^a | 6.5 ^a | 10.2 ^a |
| Butyraldehyde, butanal | 14.7 | 9.8 | 5.1, 7.2 ^a |
| Butyronitrile | 15.3 ^a | 12.5 ^a | 5.1 ^a |
| Carbitol [®] , 2-(2-ethoxyethoxy)ethanol | 16.2 | 9.2 | 14.3 |
| Carbon disulfide | 20.5, 20.3 ^a | 0.0 | 0.6, 0.0 ^a |
| Castor oil | 15.6 | 2.9 | 9.2 |
| Cellosolve [®] , 2-ethoxyethanol | 16.2 | 9.2 | 14.3 |
| Cellosolve [®] acetate, 2-ethoxyethyl acetate | 16.0 | 4.7 | 10.6 |
| Chlorobenzene | 18.6, 19.0 ^a | 4.3 | 4.1, 2.0 ^a |
| Chlorobromomethane | 17.4 | 5.7 | 3.5 |
| Chlorodifluoromethane | 12.3 ^a | 6.3 ^a | 5.7 ^a |
| Chlorofluoroethane | 11.9 ^a | 5.7 ^a | 4.1 ^a |
| Chloromethane | 15.3 ^a | 6.1 ^a | 3.9 ^a |
| 1-Chloropropane | 16.0 ^a | 7.8 ^a | 2.0 ^a |
| 3-Chloropropanol | 17.6 ^a | 5.7 ^a | 14.7 ^a |
| Cresol, methylphenol | 18.0 | 5.1 | 12.9 |
| Cyclohexane | 16.7 | 0.0 | 0.0 |
| Cyclohexanol | 17.4 | 4.1 | 13.5 |
| Cyclohexanone | 17.8 | 6.3, 8.4 ^a | 5.1 |
| Cyclohexylamine | 17.4 ^a | 3.1 ^a | 6.5 ^a |
| Cyclohexyl chloride | 19.4 ^a | 5.5 ^a | 2.0 ^a |
| 1-Decanol | 16.0 ^a | 3.5 ^a | 8.2 ^a |
| Diacetone alcohol | 15.8 | 8.2 | 10.8 |
| Dibenzyl ether | 17.4 | 3.7 | 7.4 |
| Diisobutyl ketone | 16.0 | 3.7 | 4.1 |
| Dibutyl phthalate | 16.8 | 8.6 | 4.1 |
| Dibutyl sebacate | 13.9 | 4.5 | 4.1 |
| <i>o</i> -Dichlorobenzene | 19.2 | 6.3 | 3.3 |

TABLE 12 (continued)
Hansen Parameters for Liquids, Refrigerants, and Liquid Mixtures at 25°C, Based
on 1967 Data

| Liquids | $\delta/\text{MPa}^{1/2}$ | | |
|---|---------------------------|-------------------------|------------------------|
| | δ_d | δ_p | δ_h |
| 2,2-Dichlorodiethyl ether | 18.8 ^a | 9.0 ^a | 3.1 ^a |
| Dichlorodifluoromethane | 12.3 ^a | 2.0 ^a | 0.0 ^a |
| 1,1-Dichloroethane | 16.6 ^a | 8.2 ^a | 0.4 ^a |
| 1,2-Dichloroethane, ethylene dichloride | 18.8 | 5.3 | 4.1 |
| Dichloroethylene | 17.0 | 4.7 | 7.2 |
| Dichloromethane, methylene dichloride | 18.2 | 6.3 | 6.1 |
| 1,2-Dichlorotetrafluoroethane | 12.7 ^a | 1.8 ^a | 0.0 ^a |
| Diethylamine | 14.9 ^a | 2.3 ^a | 6.1 ^a |
| 1,4-Diethylbenzene | 17.8 ^a | 0.0 ^a | 0.6 ^a |
| Diethyl carbonate | 16.6 ^a | 3.1 ^a | 6.1 ^a |
| Diethylene glycol, 2-hydroxyethyl ether | 16.2, 15.8 ^a | 14.7 | 20.5 |
| Diethylene triamine | 16.8 ^a | 13.3 ^a | 14.3 ^a |
| Diethyl ether, 1,1'-oxybisethane | 14.5 | 2.9, 4.9 ^a | 5.1, 2.0 ^a |
| Diethyl ketone | 15.8 ^a | 7.6 ^a | 4.7 ^a |
| Diethyl sulfate | 15.8 | 14.7 | 7.2 |
| Diethyl sulfide | 16.0 ^a | 6.3 ^a | 2.0 ^a |
| Difluoroethane | 9.2 ^a | 10.2 ^a | 5.7 ^a |
| Dimethoxymethane, formal, methylal | 15.1 ^a | 1.8 ^a | 8.6 ^a |
| <i>N,N</i> -Dimethylformamide | 17.4, 17.0 ^a | 13.7, 13.3 ^a | 11.3, 9.2 ^a |
| 1,1-Dimethylhydrazine | 15.3 | 5.9 | 11.1 |
| Dimethyl siloxane | 12.1 | 0.0 | 0.0 |
| Dimethylsulfone | 19.0 ^a | 19.4 ^a | 12.3 ^a |
| Dimethylsulfoxide | 18.4 | 16.4 | 10.2 |
| Dioctyl phthalate | 16.6 | 7.0 | 3.1 |
| 1,4-Dioxane, diethylene oxide | 19.0, 17.6 ^a | 1.8, 8.6 ^a | 7.4, 4.1 ^a |
| Diphenyl, 1,1'-biphenyl | 21.5 | 1.0 | 2.1 |
| Dipropylamine | 15.3 ^a | 1.4 ^a | 4.1 ^a |
| Dipropylene glycol | 16.0 ^a | 13.3 ^a | 23.9 ^a |
| Epichlorohydrin | 19.0 ^a | 10.2 ^a | 3.7 ^a |
| Ethanol | 15.8 | 8.8 | 19.4 |
| Ethanolamine | 17.2 ^a | 15.6 ^a | 21.3 ^a |
| Ethyl acetate | 15.1, 15.3 ^a | 5.3 | 9.2 |
| Ethylbenzene | 17.8 | 1.0, 0.6 ^a | 3.1, 1.4 ^a |
| 2-Ethylbutanol | 15.8 ^a | 4.3 ^a | 13.5 ^a |
| Ethyl carbonate | 19.4 ^a | 21.7 ^a | 5.1 ^a |
| Ethyl chloroformate | 15.6 | 10.0 | 6.8 |
| Ethyl cinnamate | 18.4 | 8.2 | 4.1 |
| Ethylene glycol, 1,2-ethanediol | 17.0, 16.8 ^a | 11.1 | 26.0 |
| Ethyl formate | 15.5 ^a | 8.4 ^a | 8.4 ^a |
| 2-Ethylhexanol | 16.0 ^a | 3.3 ^a | 11.9 ^a |
| Ethyl lactate | 16.0 ^a | 7.6 ^a | 12.5 ^a |
| Formamide | 17.2 ^a | 26.2 ^a | 19.0 ^a |
| Furan | 17.8 ^a | 1.8 ^a | 5.3 ^a |
| Furfural, 2-furancarboxyaldehyde | 16.8 | 14.9 | 5.1 |
| Furfuryl alcohol, 2-furanmethanol | 17.4 | 7.6 | 15.1 |
| Glycerol, 1,2,3-propanetriol | 17.4 | 12.1 | 29.3 |
| Heptane | 15.3 | 0.0 | 0.0 |
| Hexane | 14.7, 14.9 ^a | 0.0 | 0.0 |
| 1-Hexanol | 15.8 ^a | 4.3 ^a | 13.5 ^a |
| Hexylene glycol | 15.8 | 8.4 | 17.8 |
| Isoamyl acetate | 15.3 | 3.1 | 7.0 |
| Isobutyl acetate | 15.1 ^a | 3.7 ^a | 6.3 ^a |
| Isobutyl isobutyrate | 15.1 ^a | 2.9 ^a | 5.9 ^a |

TABLE 12 (continued)
 Hansen Parameters for Liquids, Refrigerants, and Liquid Mixtures at 25°C, Based
 on 1967 Data

| Liquids | $\delta/\text{MPa}^{1/2}$ | | |
|---|---------------------------|-----------------------|-------------------------|
| | δ_d | δ_p | δ_a |
| Isohexanol | 15.8 | 4.3 | 13.5 |
| Isononyl phenol | 16.6 | 4.1 | 9.2 |
| Isononyl phenoxyethanol | 16.8 | 10.2 | 8.4 |
| Isooctane, 2,2,4-trimethylpentane | 14.3 | 0.0 | 0.0 |
| Isopentane, 2-methylbutane | 13.7 | 0.0 | 0.0 |
| Isophorone | 16.6 ^a | 8.2 ^a | 7.4 ^a |
| Mesityl oxide | 16.4 ^a | 7.2 ^a | 6.1 ^a |
| Methanol, methyl alcohol | 15.4, 15.1 ^a | 12.3 | 22.3 |
| Methoxymethanol | 16.2 ^a | 9.2 ^a | 16.4 ^a |
| Methyl acetate | 15.6 | 7.2 | 7.6 |
| Methyl amyl ketone | 16.0 | 5.7 | 4.1 |
| Methyl Carbitol [®] , 2-(2-methoxyethoxy)ethanol | 16.2 ^a | 7.8 ^a | 12.7 ^a |
| Methyl Cellosolve [®] , 2-methoxyethanol | 16.2 ^a | 9.2 ^a | 16.4 ^a |
| Methyl ethyl ketone, 2-butanone | 16.0 | 9.0 | 5.1 |
| Methyl isoamyl ketone | 16.0 ^a | 5.7 ^a | 4.1 ^a |
| Methyl isobutyl carbinol, 1,2-dimethylpropanol | 15.3 ^a | 3.3 ^a | 12.3 ^a |
| Methyl isobutyl ketone, 4-methyl-2-pentanone | 15.3 | 6.1 | 4.1, 5.7 ^a |
| Methyl oleate | 14.5 | 3.9 | 3.7 |
| N-Methyl-2-pyrrolidone | 18.0 ^a | 12.3 ^a | 14.6 ^a |
| Morpholine | 18.8 ^a | 4.9 ^a | 9.2 ^a |
| Naphthalene | 19.2 | 2.1 | 5.9 |
| Nitrobenzene | 17.6 | 12.3 | 4.1 |
| Nitroethane | 16.0 ^a | 15.5 ^a | 4.5 ^a |
| Nitromethane | 15.8 | 18.8 | 5.1 |
| 2-Nitropropane | 16.2 ^a | 12.1 ^a | 4.1 ^a |
| Octane | 15.3 ^a | 0.0 ^a | 0.0 ^a |
| 1-Octanol | 16.2 ^a | 7.0 ^a | 10.6 ^a |
| Oleic acid | 14.3 | 3.1 | 5.5 |
| Oleyl triethylene glycol ether | 13.3 | 3.1 | 8.4 |
| Pentane | 14.3 ^a | 0.0 ^a | 0.0 ^a |
| 1-Pentanol | 16.0 ^a | 4.5 ^a | 13.9 ^a |
| Phenol | 18.0 | 5.9 | 14.9 |
| Phenoxyethanol | 17.8 | 5.3 | 12.3 |
| 1-Propanol | 16.0 | 6.8, 6.1 ^a | 17.4, 17.6 ^a |
| 2-Propanol | 15.8, 15.5 ^a | 7.2, 9.0 ^a | 16.0, 16.8 ^a |
| Propionitrile | 15.3 ^a | 12.3 ^a | 8.2 ^a |
| Propylamine | 15.5 ^a | 4.1 ^a | 11.3 ^a |
| Propylene carbonate | 20.1 | 18.0 | 4.1 |
| Propylene glycol, propanediol | 16.8 | 9.4 | 23.3 |
| Pyridine | 19.0 | 8.8 | 5.9 |
| 2-Pyrrolidone | 19.4 ^a | 17.4 ^a | 11.3 ^a |
| Resorcinol, 1,3-benzenediol | 18.0 | 8.4 | 21.1 |
| Stearic acid, octadecanoic acid | 16.4 | 3.3 | 5.5 |
| Styrene, ethenylbenzene | 18.6 | 1.0 | 4.1 |
| Succinic anhydride | 18.6 | 19.2 | 16.6 |
| Tetrachloroethane | 18.8 | 4.1 | 2.3 |
| Tetrachloroethylene | 19.0 | 6.6 | 2.9 |
| Tetrachloromethane, carbon tetrachloride | 17.8 | 0.0 | 0.6 |
| Tetrahydrofuran | 16.8 ^a | 5.7 ^a | 8.0 ^a |
| Tetrahydronaphthalene | 19.2 ^a | 2.0 ^a | 2.9 ^a |
| Toluene, methylbenzene | 18.0 | 1.4 | 2.1 |
| Tribromomethane, bromoform | 17.8 | 4.1 | 10.8 |
| Tributyl phosphate | 16.4 | 6.3 | 4.3 |

TABLE 12 (continued)
Hansen Parameters for Liquids, Refrigerants, and Liquid Mixtures at 25°C, Based
on 1967 Data

| Liquids | $\delta/\text{MPa}^{1/2}$ | | |
|---|---------------------------|------------|------------|
| | δ_d | δ_p | δ_h |
| Trichloroethane | 17.0 | 4.3 | 2.1 |
| Trichloroethylene | 18.0 | 3.1 | 5.3 |
| Trichloromethane, chloroform | 17.8, 17.6 ^a | 3.1 | 5.7 |
| Tricresyl phosphate | 19.0 | 12.3 | 4.5 |
| Triethylene glycol | 16.0 | 10.4 | 18.6 |
| Water | 12.3 | 31.3 | 34.2 |
| <i>o</i> -Xylene, 1,2-dimethylbenzene | 17.8 | 1.0 | 3.1 |
| Refrigerants | | | |
| R11, CCl ₃ F, trichlorofluoromethane | 15.3 | 2.1 | 0.0 |
| R12, CCl ₂ F ₂ , dichlorodifluoromethane | 12.3 | 2.1 | 0.0 |
| R13, CClF ₃ , chlorotrifluoromethane | 4.9 | 1.8 | 0.0 |
| R21, CCl ₂ FH, dichlorofluoromethane | 15.8 | 3.1 | 5.7 |
| R22, CClF ₂ H, chlorodifluoromethane | 12.3 | 6.3 | 5.7 |
| R40, CClH ₃ , chloromethane | 15.6 | 6.1 | 3.9 |
| R113, C ₂ Cl ₂ F ₃ , 1,1,2-trichloro-1,2,2-trifluoroethane | 14.7 | 1.6 | 0.0 |
| R114, C ₂ Cl ₂ F ₄ , 1,2-dichlorotetrafluoroethane | 12.7 | 1.8 | 0.0 |
| R115, C ₂ ClF ₃ , chloropentafluoroethane | 9.8 | 1.8 | 0.0 |
| R13B1, CBrF ₃ , bromotrifluoromethane | 9.6 | 2.5 | 0.0 |
| R142b, C ₂ ClF ₂ H ₃ , chlorodifluoroethane | 11.9 | 5.7 | 4.1 |
| R152a, C ₂ F ₂ H ₄ , difluoroethane | 9.2 | 10.2 | 5.7 |
| C318, C-C ₄ F ₈ , perfluorocyclobutane | 11.7 | 1.2 | 0.0 |
| Liquid Mixtures | | | |
| ASTM fuel 'A', isooctane, 2,2,4-trimethylpentane | 14.3 | 0.0 | 0.0 |
| ASTM fuel 'B' | 15.3 | 0.4 | 0.6 |
| ASTM fuel 'C' (calculated) | 16.2 | 0.8 | 1.0 |
| ASTM oil #1 | 13.9 | 0.0 | 0.0 |
| ASTM oil #2 | 15.6 | 0.6 | 0.2 |
| ASTM oil #3 | 16.6 | 1.0 | 0.4 |
| Auto brake fluid | 15.8 | 6.1 | 10.2 |
| Auto transmission fluid | 14.3 | 0.4 | 0.6 |
| Linseed oil | 13.9 | 3.5 | 3.7 |
| MIL-L-7808 (ester) | 14.3 | 2.9 | 3.1 |
| MIL-H-8446 (silicate) | 14.5 | 6.1 | 7.6 |
| MIL-H-5606 (Petr.) | 14.7 | 0.8 | 0.6 |
| Motor oil-SAE 20W | 14.7 | 0.4 | 0.4 |
| Neats foot oil | 14.3 | 2.9 | 3.7 |
| Phosphate hydraulic | 14.5 | 10.4 | 4.5 |
| Sperm oil | 14.3 | 2.1 | 2.7 |
| Turpentine | 16.4 | 1.4 | 0.4 |
| Water-glycol hydraulic fluid | 14.3 | 18.8 | 22.5 |

^a From Gardon and Teas where the values differ from those of Beerbower and Dickey.

Adapted from Beerbower, A. and Dickey, J. R., *Am. Soc. Lubric. Eng. Trans.*, 12, 1, 1969, with alternative and additional values from Gardon, J. L. and Teas, J. P., in *Treatise on Coatings*, Vol. 2, *Characterization of Coatings: Physical Techniques*, Part II, Myers, R. R. and Long, J. S., Eds., Marcel Dekker, New York, 1976, chap. 3.

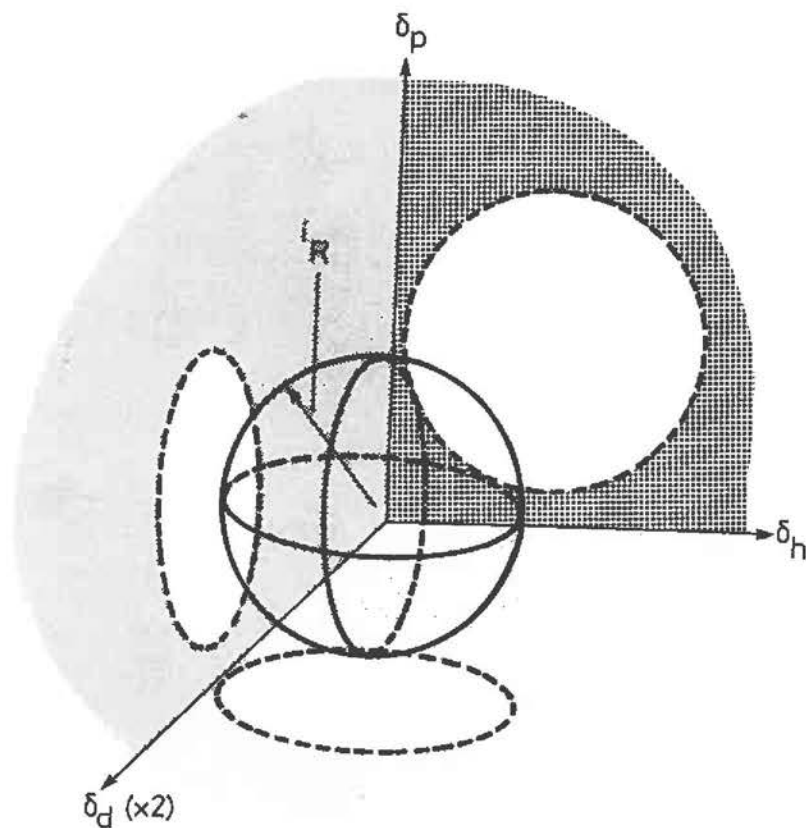


FIGURE 5. Representation of a Hansen parameter solubility sphere and its projections on three axial planes. (Adapted from Beerbower, A. and Dickey, J. R., *Am. Soc. Lubric. Eng. Trans.* 12, 1, 1969.)

found to work well, despite the fact that Equation 55 is very different from the more theoretically justified Equation 21. The "sphere" can be projected onto the three planes passing through two axes and the origin, to provide circles in two-dimensional graphs, as illustrated in Figure 5. Hansen parameters also are related to component free energies of surfaces (Section 17.3).¹²⁰

The incorporation of the numerical factor 4 in Equation 55 does not appear necessary to provide spherical interaction volumes;^{121,122} the apparent non-spherical representations which were observed were the result of the restricted range of δ_d values compared with the δ_p and δ_h ranges, and an equation based on Equation 54 is just as satisfactory:

$${}^i u_r = {}^i A^{1/2} = [({}^i \delta_d - {}^j \delta_d)^2 + ({}^i \delta_p - {}^j \delta_p)^2 + ({}^i \delta_h - {}^j \delta_h)^2]^{1/2} \quad (57)$$

Hansen¹⁵⁵ has also defined the *relative energy difference* as the ratio ${}^i u_r / R$, so if this number is less than 1.0, liquid i is predicted to be a solvent for j , with values greater than unity indicating progressively poorer solvents. Applications to several materials of biological interest appear in Table 12a.

Brench^{123,124} proposed for component i in a mixture with effective Hansen parameters $\bar{\delta}_d$, $\bar{\delta}_p$, and $\bar{\delta}_h$ the relationship

$${}^i A = ({}^i \delta_d - \bar{\delta}_d)^2 + {}^i b [({}^i \delta_p - \bar{\delta}_p)^2 + ({}^i \delta_h - \bar{\delta}_h)^2] \quad (58)$$

TABLE 12a
Hansen Parameters for Some Biological Materials, for Use
With the 1971 Hansen Liquid Parameters of Table 11

| | $\delta/\text{MPa}^{1/2}$ | | | | |
|----------------------------|---------------------------|------------|------------|------------|----------|
| | δ_d | δ_p | δ_h | δ_l | $\sum R$ |
| Lard, 23°C | 17.8 | 2.7 | 4.4 | 18.4 | 8.0 |
| Lard, 37°C | 15.9 | 1.2 | 5.4 | 16.8 | 12.0 |
| Water* | 15.1 | 20.4 | 16.5 | 30.3 | 18.1 |
| Blood serum | 23.2 | 22.7 | 30.6 | 44.6 | 20.5 |
| Sucrose | 21.7 | 26.3 | 29.6 | 45.1 | 20.4 |
| Urea | 20.9 | 18.7 | 26.4 | 38.5 | 19.4 |
| Keratin (psoriasis scales) | 24.6 | 11.9 | 12.9 | 30.3 | 19.0 |
| Lignin | 20.6 | 13.9 | 15.3 | 29.2 | 11.8 |

* For 1% solutions in water; preferred value, amines not included.

Adapted from Hansen, C. M. and Anderson, B. H., *Am. Ind. Hyg. Assoc.*, 49, 301, 1988.

where b_i is a Hansen weighting factor, a property of component i , with values (Table 13) comparable to those of b_j in Table 10. These values have been interpreted physically¹²⁴ on the basis that the dispersion forces represent a "billiard ball" effect over the whole molecule, while the polar and hydrogen-bonding terms are localized on groups and thus not uniformly distributed.

Numerical results for polymers are quoted in Section 14.5, together with the application of vector methods to the interaction of liquid mixtures with polymers. Hansen parameters are applied to solid solubilities in Chapter 12. In some applications, only two of the three Hansen parameters are used, so that the locations of liquids may be displayed on two-dimensional, projected maps. Figure 6 shows the range of δ_p versus δ_h locations for major liquid groups, regions of overlap predicting mutual miscibility; this technique may be applied to the formulation of extraction systems.¹²⁵ Solubility ranges for polymers may be represented in the same way (Section 15.1).

The original "Hansen parameters" were determined as outlined above, but very similar parameters have been obtained by alternative calculation methods,¹²⁶ as indicated in Section 5.11, with Hoy's major set of values being reported below in Table 17.

There is considerable variation in the Hansen parameters reported for water (Table 14). A study of the solubilities of a variety of *organic compounds in water*^{26,155} provides the values in the last three entries of this Table. The δ_h and δ_l values are considerably lower than and inconsistent with those previously reported, which appear to be appropriate for solutions of *water in organic liquids*. (Grunwald¹²⁷ discussed aqueous solutions in terms of components described as "isodelphic" (unchanged thermodynamic state of solvent during the solution process) and "lyodelphic" (partial molar contributions due to solute perturbation of solvent network). Use of the regular solution model gave a water total cohesion parameter of 29 MPa^{1/2}, consistent with the "organics in water" value.) This variability in Hansen parameter values is a fundamental problem associated with the use of δ_h rather than the more appropriate δ_a and δ_b to represent the hydrogen-bonding cohesion, and attempts to reconcile the divergent δ_h values are futile. The reservations originally expressed by Tawn¹²⁸ on Hansen parameters are still valid: this method of describing interactions between liquids and potential solutes is neither as simple as the Burrell method (Sections 4.5, 14.3) nor as complete as a full set of component cohesion parameters. However, the recent values provided by Hansen¹⁵⁵ for "1% solutions in water" (Table 12a) acknowledge the problem and provide a guide to behavior in hydrogen-bonded systems. Clearly the use of separate Lewis acid

TABLE 13
Values of Hansen Weighting
Factor

| Liquid | δ_b |
|---------------------------------|------------|
| Hydrocarbons | |
| Hexane | 0.22 |
| Heptane | 0.20 |
| Isooctane | 0.17 |
| Cyclohexane | 0.19 |
| Benzene | 0.15 |
| Toluene | 0.064 |
| Ethylbenzene | 0.12 |
| Styrene | 0.13 |
| Chlorinated Hydrocarbons | |
| Trichloromethane | 0.22 |
| Tetrachloromethane | 0.24 |
| Trichloroethylene | 0.20 |
| Tetrachloroethylene | 0.24 |
| 1,1,2-Trichloroethane | 0.18 |
| Ketones | |
| Acetone | 0.14 |
| Methyl ethyl ketone | 0.14 |
| Methyl isobutyl ketone | 0.13 |
| Esters | |
| Methyl acetate | 0.16 |
| Ethyl acetate | 0.14 |
| Propyl acetate | 0.16 |
| Butyl acetate | 0.19 |
| Amyl acetate, pentyl acetate | 0.19 |
| Ethyl propionate | 0.20 |
| Ethyl butyrate | 0.19 |
| Alcohols | |
| Methanol | 0.26 |
| Ethanol | 0.20 |
| 1-Propanol | 0.24 |
| 2-Propanol | 0.20 |
| 1-Butanol | 0.24 |
| 2-Butanol | 0.19 |
| Isobutanol | 0.23 |
| <i>tert</i> -Butanol | 0.20 |
| 1-Pentanol | 0.19 |
| 1-Hexanol | 0.28 |
| <i>sec</i> -Octanol | 0.23 |
| Ethylene glycol | 0.31 |
| Glycerol | 0.20 |
| Carboxylic Acid | |
| Acetic acid | 0.12 |

TABLE 13 (continued)
Values of Hansen Weighting
Factor

| Liquid | i_b |
|------------------------------------|-------|
| Nitrogen-Containing Liquids | |
| Ethylenediamine | 0.29 |
| Pyridine | 0.11 |
| Lipids | |
| Dioclein | 0.20 |
| Triolein | 0.16 |
| Trilinolein | 0.17 |
| Olive oil | 0.18 |
| Oleic acid | 0.18 |
| Other Liquids | |
| 1,4-Dioxane | 0.10 |
| Furfural | 0.26 |
| Propylene carbonate | 0.41 |
| Water | 0.32 |

Adapted from Ashton, N. F., McDermott, C., and Brench, A., in *Handbook of Solvent Extraction*, Lo, T. C., Baird, M. H. I., and Hanson, C., Eds., John Wiley & Sons-Interscience, New York, 1983, 3.

and Lewis base component parameters would be superior, but more cumbersome, in providing an approximate representation of the "unsymmetrical" interactions.

5.10 FRACTIONAL THREE-COMPONENT COHESION PARAMETERS

Teas¹²⁹ showed that for several polymer-liquid systems it is possible to use *fractional cohesive pressures* plotted on a triangular chart to represent miscibility limits:

$$U_d/U = \delta_d^2/\delta_c^2; U_p/U = \delta_p^2/\delta_c^2; U_h/U = \delta_h^2/\delta_c^2 \quad (59)$$

where

$$\delta_c^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (60)$$

and

$$U = U_d + U_p + U_h \quad (61)$$

This method was used by Vial^{130,131} (Table 15), but Teas^{119,129,132} chose instead to use *fractional cohesion parameters*, which may be defined

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h}; f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h}; f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \quad (62)$$

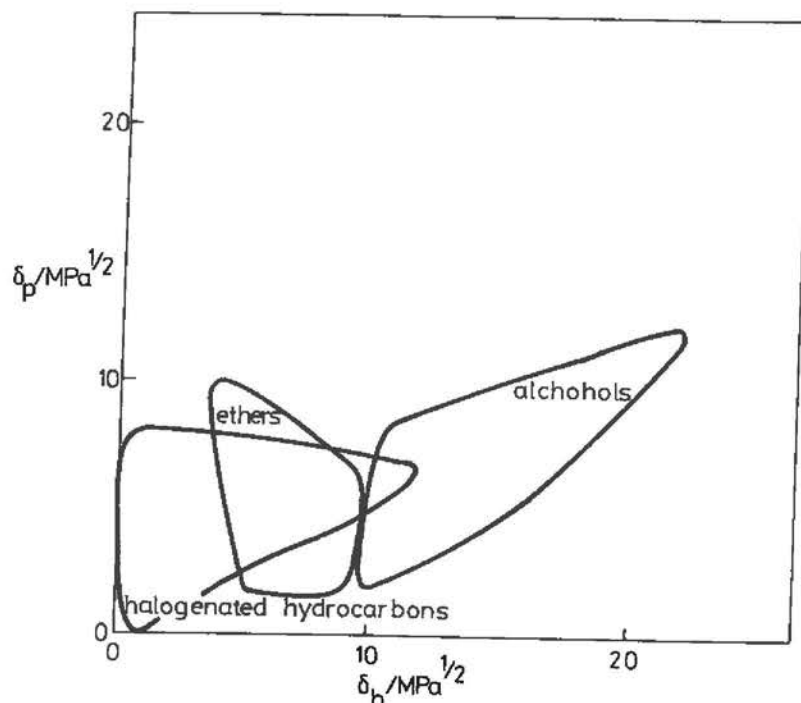


FIGURE 6. Hansen parameter $\delta_p - \delta_h$ locations for major liquid groups: (A) ethers, halogenated hydrocarbons, and alcohols; (B) esters, aromatic hydrocarbons, ketones, and phenols; (C) aldehydes, polyhydric alcohols, unionized acids, and alkanes; and (D) proton donors (acids, phenols, amines, alcohols, polyhydric alcohols). (Adapted from Klein, E., Eichelberger, J., Eyer, C., and Smith, J., *Water Res.*, 9, 807, 1975.)

The fractional cohesion parameters of Gardon and Teas¹¹⁹ in Table 16 are calculated from the data published by Hansen and Skaarup in 1967; also included are the values of Teas^{28,129} based on Hansen's earlier publication,¹⁰ as these have been widely used. The fractional cohesion parameters defined in Equation 62 have the advantage of spreading the data points more uniformly over the triangular chart, but the disadvantage that they are completely empirical, without even the limited theoretical justification of Hansen parameters. Examples of fractional maps for polymers are shown in Figures 16 to 33, Chapter 15.

The triangular representations make the simplifying assumption that the total cohesion parameter, δ_t , is constant for all materials, and that the *relative* magnitudes of the three contributions (dispersion forces, polar interactions, hydrogen bonding) determine the extent of miscibility. Inspection of tables of Hansen parameter values shows that although there is much greater variation in δ_p and δ_h than in δ_t , the total cohesion parameter is not even approximately constant.

5.11 OTHER TWO- AND THREE-COMPONENT COHESION PARAMETERS

If it is assumed that the cohesive energy ($-U$) is made up of an additive combination of contributions from nonpolar or dispersive interactions ($-U_d$), polar interactions ($-U_p$), and hydrogen-bonding or similar specific association interactions ($-U_h$),

$$-U = -U_d - U_p - U_h \quad (63)$$

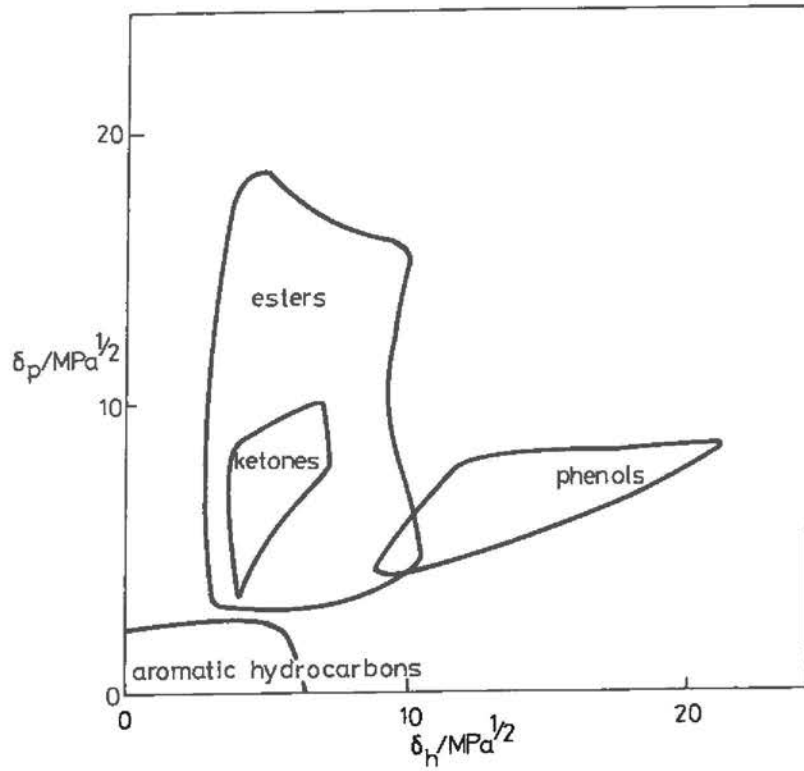


FIGURE 6B.

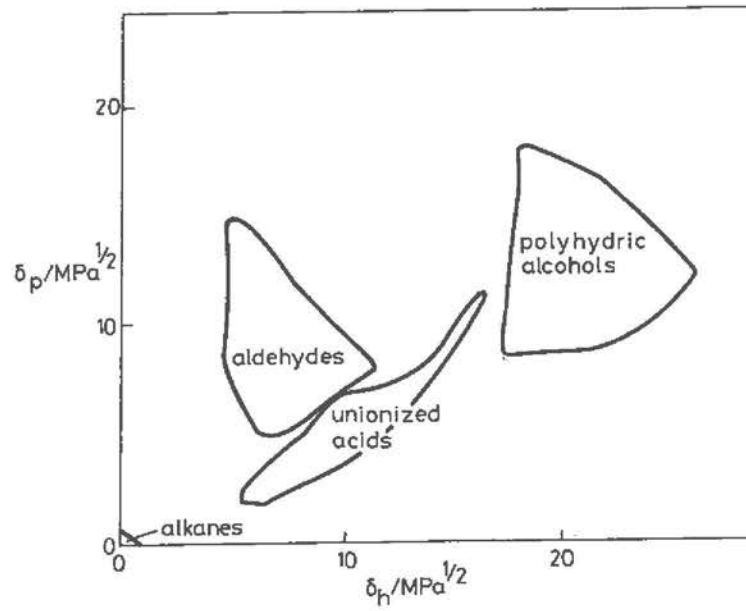


FIGURE 6C.

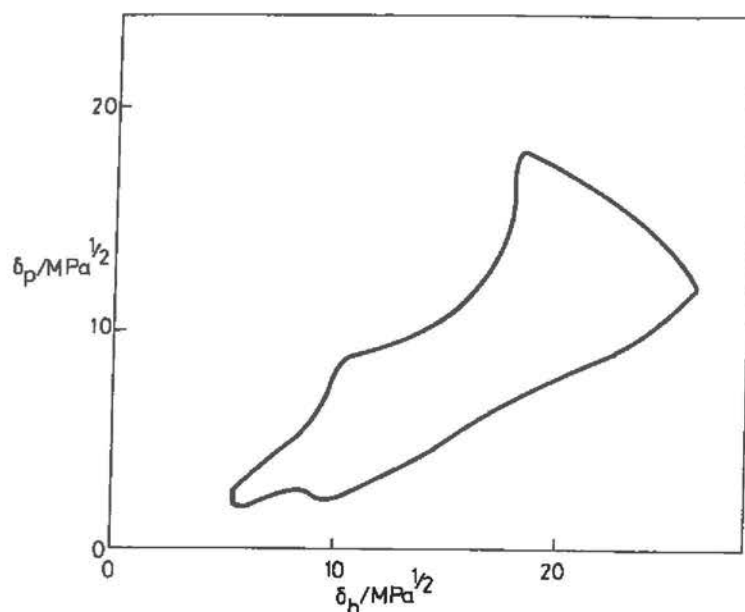


FIGURE 6D.

TABLE 14
Hansen Parameters for Water

| $\delta/\text{MPa}^{1/2}$ | | | | | Source | Ref. |
|---------------------------|------------|------------|------------|------------|-------------------------------------|-------------|
| δ_d | δ_p | δ_h | δ_t | δ_r | | |
| 12 | 23 | 40 | 48 | — | Table 18 | 126 |
| 12 | 31 | 34 | 48 | — | Table 12 | 10, 11, 118 |
| 16 | 16 | 42 | 48 | — | Table 11 | 25 |
| 20 | 18 | 18 | 32 | 15 | Organic liquids in water | 26 |
| 15 | 20 | 17 | 30 | 18 | 1% solutions in water, Table 12a | 155 |
| — | — | — | 33—36 | — | Aqueous phase in solvent extraction | 158 |
| — | — | — | 29 | — | Grunwald | 127 |

then it follows that the corresponding cohesive pressures and cohesion parameters can be defined so that

$$-U/V = -U_d/V - U_p/V - U_h/V \quad (64)$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (65)$$

as seen in Equation 54, and

$${}^vA = ({}^i\delta_d/{}^j\delta_d - {}^j\delta_d)^2 + ({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2 \quad (66)$$

This method was developed by Hansen^{9-30,155} (Section 5.10) on an empirical basis and by means of semiempirical equations^{28,117,120} but it may also be used for theoretical subdivisions of the Hildebrand parameter with other bases. With the aid of relationships of the type indicated in Section 8.2, the Hansen parameters can be described in terms of molecular parameters related to intermolecular forces and molecular sizes.¹³³

Null and Palmer^{111,134,135} extended the polar-nonpolar cohesion parameter concept of

TABLE 15
Fractional Cohesive Pressures in Order of Increasing Total Value

| Liquid | $\delta_c/\text{MPa}^{1/2}$ | 100 U_d/U | 100 U_p/U | 100 U_h/U |
|--|-----------------------------|-------------|-------------|-------------|
| Hexane | 14.8 | 100.0 | 0.0 | 0.0 |
| Diethyl ether | 15.6 | 85.8 | 3.4 | 10.8 |
| Diisobutyl ketone | 16.7 | 89.3 | 4.8 | 5.9 |
| Cyclohexane | 16.7 | 100.0 | 0.0 | 0.0 |
| Isoamyl acetate | 17.0 | 80.1 | 3.2 | 16.7 |
| Butyl acetate | 17.3 | 82.1 | 4.5 | 13.4 |
| 1,1,1-Trichloroethane | 17.5 | 92.6 | 6.0 | 1.4 |
| Methyl isobutyl ketone | 17.5 | 81.2 | 13.0 | 5.8 |
| Tetrachloromethane, carbon tetrachloride | 17.7 | 100.0 | 0.0 | 0.0 |
| Toluene, methylbenzene | 18.2 | 98.1 | 0.6 | 1.3 |
| Ethyl acetate | 18.6 | 67.2 | 8.2 | 24.6 |
| Benzene | 18.7 | 98.5 | 0.3 | 1.2 |
| Trichloromethane, chloroform | 18.8 | 88.1 | 2.6 | 9.3 |
| Methyl ethyl ketone, 2-butanone | 19.0 | 70.2 | 22.5 | 7.3 |
| Trichloroethylene | 19.0 | 89.5 | 2.6 | 7.9 |
| Styrene, ethenylbenzene | 19.0 | 95.1 | 0.3 | 4.6 |
| Tetrahydronaphthalene, tetralin | 19.4 | 96.7 | 1.1 | 2.2 |
| Tetrahydrofuran | 19.5 | 74.6 | 8.6 | 16.8 |
| Ethylglycol acetate | 19.6 | 65.2 | 5.7 | 29.1 |
| Acetophenone | 19.8 | 77.8 | 18.8 | 3.4 |
| Isophorone | 19.9 | 69.4 | 16.9 | 13.7 |
| 1,4-Dioxane | 19.9 | 86.3 | 0.8 | 12.9 |
| 1,2-Dichloroethane, ethylene dichloride | 20.0 | 88.7 | 7.1 | 4.2 |
| Acetone, 2-propanone | 20.0 | 60.5 | 27.4 | 12.1 |
| Cyclohexanone | 20.2 | 76.4 | 17.2 | 6.4 |
| Dichloromethane, methylene dichloride | 20.3 | 81.0 | 9.8 | 9.2 |
| 2-Nitropropane | 20.5 | 61.6 | 34.4 | 4.0 |
| Pyridine | 21.7 | 76.1 | 16.4 | 7.5 |
| Nitrobenzene | 21.7 | 64.9 | 31.6 | 3.5 |
| Cyclohexanol | 22.4 | 60.3 | 3.3 | 36.4 |
| Nitroethane | 22.7 | 49.3 | 46.8 | 3.9 |
| 1-Butanol | 23.1 | 47.6 | 6.1 | 46.3 |
| Acetonitrile | 24.0 | 39.4 | 54.3 | 6.3 |
| 1-Propanol | 24.5 | 41.9 | 7.6 | 50.5 |
| Methylglycol | 24.7 | 42.6 | 13.8 | 43.6 |
| N,N-Dimethylformamide | 24.8 | 49.1 | 30.4 | 20.5 |
| Nitromethane | 25.2 | 39.5 | 56.3 | 4.2 |
| Ethanol | 26.4 | 35.5 | 11.0 | 53.5 |
| Dimethylsulfoxide | 26.4 | 47.6 | 37.6 | 14.8 |
| 1,3-Butanediol | 28.9 | 32.8 | 12.0 | 55.2 |
| Methanol | 29.2 | 26.2 | 17.2 | 56.6 |
| Diethylene glycol | 29.9 | 28.9 | 24.3 | 46.8 |
| Ethanolamine | 31.7 | 29.6 | 24.5 | 45.9 |
| Glycol | 33.3 | 26.3 | 11.3 | 62.4 |
| Formamide | 36.4 | 22.0 | 51.0 | 27.0 |
| Water | 48.1 | 6.6 | 42.6 | 50.8 |

Adapted from Vial, J., *C.R. Acad. Sci. Ser. C*, 270, 683, 1970; and Thesis, Faculty of Science, Paris, 1970.

Section 5.8 by defining a parameter described here as δ_g to represent the cohesive pressure due to association or hydrogen bonding:

$$\delta_t^2 = \delta_\lambda^2 + \delta_r^2 + \delta_g^2 \quad (67)$$

Comparison of Equations 65 and 67 with the five-parameter Equation 24 suggests

TABLE 16
Fractional Hansen Parameters of Liquids, Plasticizers and Oils

| Compound | $\delta_r/\text{MPa}^{1/2}$ | $100f_d$ | $100f_p$ | $100f_h$ |
|---|-----------------------------|----------|----------|----------|
| Liquids | | | | |
| Acetic acid, ethanoic acid | (21.2) | (40) | (19) | (41) |
| Acetic anhydride | (22.2) | (36) | (37) | (27) |
| Acetone, 2-propanone | 20.1 | 47(50) | 32(37) | 21(13) |
| Acetonitrile | 24.6 | 39(41) | 45(43) | 16(16) |
| Acetophenone, 1-phenylethanone | 19.8 | 59(58) | 29(25) | 12(17) |
| Acetyl chloride | 19.4 | 52 | 35 | 13 |
| Acrylonitrile, 2-propenenitrile | 21.7 | 41 | 43 | 16 |
| Aniline | 24.6(22.6) | 50(55) | 19(21) | 31(24) |
| Benzaldehyde | 21.3 | 61(57) | 23(16) | 16(27) |
| Benzene | 18.8 | 78(76) | 8(7) | 14(17) |
| Benzonitrile | 22.1 | 48 | 37 | 15 |
| Benzyl alcohol, benzenemethanol | 24.6 | 48 | 16 | 36 |
| Benzyl chloride | 20.3 | 66 | 25 | 9 |
| Biphenyl, diphenyl | 21.5 | 88 | 4 | 8 |
| Bromobenzene | 20.5 | 72 | 21 | 7 |
| Bromoethane, ethyl bromide | 18.2 | 56 | 27 | 17 |
| 1-Bromonaphthalene | 21.1 | 74(68) | 11(18) | 15(14) |
| Butane | 14.1 | 100 | 0 | 0 |
| 1,3-Butanediol | 28.8 | 34(35) | 21(17) | 45(48) |
| 1-Butanol | 23.3 | 43(43) | 15(14) | 42(43) |
| Butyl acetate | 17.4 | 60(60) | 13(16) | 17(24) |
| Butylamine, 1-butanamine | 17.6 | 59 | 14 | 27 |
| Butyl Carbitol [®] , diethylene glycol monobutyl ether | 20.1 | 46 | 18 | 36 |
| Butyl Cellosolve [®] , ethylene glycol monobutyl ether | 20.5(21.0) | 46(46) | 18(20) | 36(34) |
| Butyl lactate | 19.2 | 48(52) | 20(22) | 32(26) |
| Butyraldehyde, butanal | 18.4 | 50 | 33 | 17 |
| Butyric acid, butanoic acid | (23.1) | (53) | (13) | (34) |
| γ -Butyrolactone | 26.2 | 44(43) | 39(36) | 17(21) |
| Butyronitrile | 20.5 | 44(48) | 41(39) | 15(13) |
| Carbitol [®] , diethylene glycol monoethyl ether | 21.3 | 48 | 23 | 29 |
| Carbitol [®] acetate, diethylene glycol monoethyl ether acetate | 19.4 | 54 | 33 | 13 |
| Carbon disulfide | 20.3 | 88(86) | 8(7) | 4(7) |
| Cellosolve [®] , ethylene glycol monoethyl ether | 22.1(24.3) | 42(43) | 20(20) | 38(37) |
| Cellosolve [®] acetate, ethylene glycol monomethyl ether acetate | 19.2 | 51(50) | 15(34) | 34(16) |
| Chlorobenzene | 19.6 | 65(70) | 17(15) | 18(15) |
| 1-Chlorobutane | 17.2 | 68(66) | 24(23) | 8(11) |
| Chlorodifluoromethane, Freon 22 | 14.9 | 50 | 26 | 24 |
| Chlorofluoroethane | 14.1 | 55 | 26 | 19 |
| Chloromethane, methyl chloride | 17.0 | 61 | 24 | 15 |
| 1-Chloropropane, propyl chloride | 17.4 | 62 | 30 | 8 |
| 3-Chloropropanol | 23.7 | 46 | 15 | 39 |
| <i>m</i> -Cresol, 3-methylphenol | 22.7 | 50(49) | 14(17) | 36(34) |
| Cyclohexane | 16.8 | 94 | 2 | 4 |
| Cyclohexanol | 22.5 | 50 | 12 | 38 |
| Cyclohexanone | 20.3 | 55(56) | 28(22) | 17(22) |
| Cyclohexylamine | (18.5) | (63) | (15) | (22) |
| Cyclohexyl chloride | 19.4(18.4) | 70(68) | 21(24) | 9(8) |
| Decane | 15.8 | 100 | 0 | 0 |
| 1-Decanol | 19.2 | 58 | 13 | 29 |

TABLE 16 (continued)
Fractional Hansen Parameters of Liquids, Plasticizers and Oils

| Compound | $\delta_d/\text{MPa}^{1/2}$ | $100f_d$ | $100f_p$ | $100f_h$ |
|--|-----------------------------|----------|----------|----------|
| Diacetone alcohol | 20.3 | 45(37) | 24(29) | 31(34) |
| Dibenzyl ether | 19.2 | 61 | 13 | 36 |
| Diisobutyl ketone | 16.6 | 67 | 16 | 17 |
| <i>o</i> -Dichlorobenzene | 20.5 | 67(69) | 22(15) | 11(16) |
| 2,2-Dichlorodiethyl ether | 21.1 | 61(54) | 29(37) | 10(9) |
| Dichlorodifluoromethane, Freon 12 | 12.5 | 86 | 14 | 0 |
| 1,1-Dichloroethane | 18.4 | 66 | 33 | 2 |
| 1,2-Dichloroethane, ethylene dichloride | 20.1 | 67(63) | 19(23) | 14(14) |
| Dichloromethane, methylene dichloride | 19.8 | 59 | 21 | 20 |
| 1,2-Dichlorotetrafluoroethane, Freon 114 | 12.9 | 87 | 13 | 0 |
| Diethylamine | 16.4 | 64(62) | 10(19) | 26(19) |
| 1,4-Diethylbenzene | 18.0 | 97 | 0 | 3 |
| Diethyl carbonate | 18.0 | 64 | 12 | 24 |
| Diethyl ether, 1,1'-oxybisethane | 15.6 | 64(67) | 13(23) | 23(10) |
| Diethyl ketone, 3-pentanone | 18.2 | 56 | 27 | 17 |
| Diethyl sulfate | 22.7 | 42 | 39 | 19 |
| Diethyl sulfide | 17.4 | 77(66) | 14(26) | 9(8) |
| Diethylene glycol | 29.9 | 31(25) | 29(30) | 40(45) |
| Diethylenetriamine | 25.8 | 38 | 30 | 32 |
| Difluoroethane | 14.9 | 37 | 40 | 23 |
| Dimethoxymethane, formal, methylal | 17.4 | 59(57) | 7(32) | 34(11) |
| <i>N,N</i> -Dimethylformamide | 24.8 | 41 | 32 | 27 |
| Dimethylsiloxane | 12.1 | 100 | 0 | 0 |
| Dimethyl sulfone | 29.9 | 38 | 38 | 24 |
| Dimethylsulfoxide | 26.4 | 41(37) | 36(33) | 23(30) |
| 1,4-Dioxane, diethylene oxide | 20.7 | 67(58) | 7(28) | 26(14) |
| Dipentene | 17.4 | 75 | 20 | 5 |
| Dipropylamine | 16.2 | 74(72) | 7(12) | 19(16) |
| Dipropylene glycol, oxybispropanol | 31.7 | 35(30) | 26(25) | 39(45) |
| Epichlorohydrin, (chloromethyl)oxirane | 21.9 | 58 | 31 | 11 |
| Ethanol | 26.2 | 36(36) | 18(19) | 46(45) |
| Ethanolamine | 31.5 | 32(31) | 29(32) | 40(39) |
| Ethyl acetate | 18.4 | 51 | 18(37) | 31(17) |
| Ethylbenzene | 18.0 | 87(80) | 3(5) | 10(15) |
| 2-Ethylbutanol | 21.3 | 48 | 10 | 42 |
| Ethyl chloroformate | 19.6 | 48 | 31 | 21 |
| Ethyl formate | 19.4 | 48 | 26 | 26 |
| 2-Ethylhexanol | 20.3 | 50(53) | 9(6) | 41(41) |
| Ethyl lactate | 21.1 | 44 | 21(23) | 35(33) |
| Ethyl carbonate | 29.7 | 42 | 47 | 11 |
| Ethylene glycol, 1,2-ethanediol | 33.3 | 30(32) | 18(17) | 52(51) |
| Formamide | 36.4 | 28 | 42 | 30 |
| Formic acid | (24.9) | (33) | (20) | (47) |
| Furfural, 2-furancarboxyaldehyde | 24.3 | 46 | 41 | 13 |
| Furan | 18.6 | 71(65) | 7(12) | 22(23) |
| Furfuryl alcohol, 2-furanmethanol | 24.3 | 43 | 19 | 38 |
| Glycerol, 1,2,3-propanetriol | 36.2(43.1) | 25(26) | 23(22) | 52(52) |
| Heptane | 15.3 | 100 | 0 | 0 |
| 1-Heptanol | 21.5 | 47 | 14 | 39 |
| Hexane | 14.9 | 100(96) | 0(2) | 0(2) |
| 1-Hexanol | 21.9 | 47 | 13 | 40 |
| Isoamyl acetate | 17.2 | 60 | 12(27) | 28(13) |
| Isobutyl acetate | 16.6 | 60 | 15 | 25 |

TABLE 16 (continued)
Fractional Hansen Parameters of Liquids, Plasticizers and Oils

| Compound | $\delta_r/\text{MPa}^{1/2}$ | 100 f_d | 100 f_p | 100 f_h |
|--|-----------------------------|-----------|-----------|-----------|
| Isobutyl isobutyrate | 16.6(16.0) | 63(63) | 12(22) | 25(15) |
| Isononyl phenol | 19.4 | 55 | 14 | 31 |
| Isophorone | 19.8 | 51(52) | 25(25) | 24(23) |
| Mesityl oxide | 18.6 | 55 | 24 | 21 |
| Methanol | 29.3 | 30(31) | 22(23) | 48(46) |
| Methoxymethanol | 24.8 | 39 | 22 | 39 |
| Methyl acetate | 19.4 | 45 | 36 | 19 |
| Methyl Carbitol [®] , diethylene glycol monomethyl ether | 22.7(22.1) | 44(44) | 21(22) | 35(34) |
| Methyl Cellosolve [®] , ethylene glycol monomethyl ether | 24.6 | 39 | 22 | 39 |
| Methyl Cellosolve [®] acetate, ethylene glycol monomethyl ether acetate | 20.3 | 46 | 17 | 37 |
| Methyl ethyl ketone, 2-butanone | (19.0) | (53) | (30) | (17) |
| Methyl formate | 20.7 | 46 | 22 | 32 |
| Methyl isoamyl ketone | 17.6 | 62(58) | 20(22) | 18(20) |
| Methyl isobutyl carbinol | 19.8 | 50(51) | 10(7) | 40(42) |
| Methyl isobutyl ketone | 17.6 | 58(56) | 22(23) | 20(21) |
| N-Methyl 2-pyrrolidone | 22.9 | 48 | 32 | 20 |
| Morpholine | 21.7 | 57(53) | 15(21) | 28(26) |
| Naphthalene | 20.3 | 70 | 8 | 22 |
| Nitrobenzene | 21.7 | 52(59) | 36(29) | 12(12) |
| Nitroethane | 22.7 | 44(47) | 43(42) | 13(11) |
| Nitromethane | 25.2 | 40(41) | 47(46) | 13(13) |
| 2-Nitropropane | 20.5 | 50(58) | 37(33) | 13(9) |
| Octane | 15.1 | 100 | 0 | 0 |
| 1-Octanol | 20.5 | 53 | 9 | 38 |
| 1-Pentanol, amyl alcohol | 22.7(21.7) | 46(47) | 13(12) | 41(41) |
| Pentane | 14.3 | 100 | 0 | 0 |
| Phenol | 24.1 | 46 | 15 | 39 |
| 1-Propanol | 24.6 | 40 | 16 | 44 |
| Propionitrile | 21.9 | 43 | 34 | 23 |
| Propyl acetate | 18.0 | 57 | 15 | 28 |
| Propylene carbonate | 27.1 | 48(48) | 38(43) | 14(9) |
| Propylene glycol, propanediol | 30.3 | 34(39) | 16(15) | 50(46) |
| Pyridine | 21.7 | 56(56) | 26(22) | 18(22) |
| 2-Pyrrolidone | 28.4 | 41 | 36 | 23 |
| Resorcinol, 1,3-benzenediol | 29.1 | 38 | 18 | 44 |
| Styrene, ethenylbenzene | 19.0 | 78(76) | 4(9) | 18(15) |
| Tetrachloroethane | 21.7 | 56 | 15 | 19 |
| Tetrachloroethylene | 20.3 | 67 | 23 | 10 |
| Tetrachloromethane, carbon tetrachloride | 17.8 | 85 | 2 | 13 |
| Tetrahydrofuran | 19.4 | 55(55) | 19(22) | 26(23) |
| Tetrahydronaphthalene, tetralin | 19.4 | 80(83) | 8(4) | 12(13) |
| Toluene, methylbenzene | 18.2 | 80(78) | 7(6) | 13(16) |
| Tribromomethane, bromoform | 21.5 | 54 | 13 | 33 |
| Trichloroethane | 17.6 | 70(68) | 19(17) | 11(15) |
| Trichloroethylene | 19.0 | 68 | 12 | 20 |
| Trichloromethane, chloroform | 17.8 | 85 | 2 | 13 |
| Triethylene glycol | 26.6 | 36 | 23 | 41 |
| Water | 48.1 | 18(19) | 28(22) | 54(58) |
| Xylene, dimethylbenzene (mixed isomers) | 18.0 | 83(82) | 5(6) | 12(12) |

TABLE 16 (continued)
Fractional Hansen Parameters of Liquids, Plasticizers and Oils

| Compound | $\delta_d/\text{MPa}^{1/2}$ | $100f_d$ | $100f_p$ | $100f_h$ |
|------------------------------|-----------------------------|----------|----------|----------|
| Plasticizers | | | | |
| Butyl stearate | 15.3 | 67 | 17 | 16 |
| Dibutyl maleate | 17.2 | 60 | 12 | 28 |
| Dibutyl phthalate | 20.1 | 57 | 29 | 14 |
| Dibutyl sebacate | 15.1 | 62 | 20 | 18 |
| Dimethyl phthalate | 22.1 | 48 | 38 | 14 |
| Dioctyl adipate | 18.2 | 64 | 23 | 13 |
| Dioctyl phthalate | 18.2 | 62 | 26 | 12 |
| Ethyl cinnamate | 20.7 | 60 | 27 | 13 |
| Methyl oleate | 15.6 | 67 | 17 | 16 |
| Tricresyl phosphate | 24.8 | 51 | 30 | 29 |
| Trimethyl phosphate | 25.4 | 39 | 37 | 24 |
| Tributyl phosphate | 18.0 | 45 | 35 | 20 |
| Trioctyl adipate | — | 62 | 24 | 14 |
| Oils and Commercial Solvents | | | | |
| Castor oil | 18.2 | 56 | 11 | 33 |
| Linseed oil (white refined) | 14.9 | 66 | 17 | 17 |
| Neats foot oil | 14.7 | 69 | 14 | 17 |
| Sperm oil | 14.5 | 75 | 11 | 14 |
| Mineral oil (white refined) | 14.5 | 100 | 0 | 0 |
| Pine oil | 16.6 | 70 | 14 | 16 |
| Cottonseed oil | 14.9 | 67 | 15 | 18 |
| Mineral spirits | — | 90 | 4 | 6 |
| VM & P naphtha | — | 94 | 3 | 3 |
| Odorless mineral spirits | — | 98 | 1 | 1 |
| Turpentine | — | 77 | 18 | 5 |

Adapted from Gardon, J. L. and Teas, J. P., *Treatise on Coatings*, Vol. 2, *Characterization of Coatings: Physical Techniques*, Part II, Myers, R. R. and Long, J. S., Eds., Marcel Dekker, New York, 1976, chap. 8. Values in parentheses are from the earlier publication of Teas, J. P., *J. Paint Technol.*, 40(516), 19, 1968, for those cases where differences occur.

$$\delta_\lambda^2 \approx \delta_a^2 \quad (68)$$

$$\delta_r^2 \approx \delta_p^2 \approx \delta_o^2 + 2\delta_i\delta_d \quad (69)$$

$$\delta_e^2 \approx \delta_b^2 \approx 2\delta_a\delta_b \quad (70)$$

The association parameter δ_e was obtained from the entropy and enthalpy of association as defined by Wiehe and Bagley,^{65,136,137} who had investigated the activity coefficients in mixtures of alcohols with nonpolar liquids and developed multiparameter equations for their correlation (Section 7.5). Wiehe, in unpublished work cited in Reference 156, also developed an alternative two-component formalism:

$$\delta^2 = \delta_c^2 + \delta_r^2$$

where δ_c is a measure of ability to form "complexes" and δ_r is a measure of ability to interact by field forces which do not depend on orientation ($\delta_r \approx \delta_d$). These cohesion parameters, which were used for solvent selection by two-dimensional mapping, are collected in Table 16a.

Hoy¹²⁶ determined nonpolar, polar, and hydrogen-bonding parameters by semi-empirical methods which involved:

TABLE 16a
Two-Component Complexing — Field Force
Cohesion Parameters for Liquids

| Liquid | $\delta/\text{MPa}^{1/2}$ | | |
|-------------------------------|---------------------------|------------|------------|
| | δ_i | δ_r | δ_c |
| Acetone | 19.7 | 15.0 | 12.8 |
| Acetonitrile | 24.8 | 15.3 | 19.5 |
| Acetophenone | 21.6 | 17.5 | 12.7 |
| Benzene | 18.7 | 18.3 | 4.0 |
| Butyl acetate | 17.8 | 15.7 | 8.3 |
| Carbon disulfide | 20.3 | 20.3 | 0.0 |
| Chlorobenzene | 19.8 | 19.2 | 4.7 |
| Cyclohexane | 16.8 | 16.8 | 0.0 |
| Cyclohexanone | 21.3 | 17.4 | 12.3 |
| Dibromomethane | 21.3 | 20.2 | 6.7 |
| <i>o</i> -Dichlorobenzene | 20.5 | 19.8 | 5.6 |
| 1,2-Dichloroethane | 20.2 | 19.2 | 6.1 |
| Dichloromethane | 20.2 | 18.2 | 8.7 |
| Dimethylsulfoxide | 26.4 | 18.4 | 19.0 |
| <i>N,N</i> -Dimethylacetamide | 22.1 | 17.4 | 13.6 |
| <i>N,N</i> -Dimethylformamide | 24.1 | 19.1 | 14.7 |
| 1,4-Dioxane | 20.7 | 18.4 | 9.5 |
| Ethyl acetate | 18.2 | 15.2 | 10.0 |
| Ethylbenzene | 18.1 | 17.9 | 2.9 |
| Heptane | 15.3 | 15.3 | 0.0 |
| Hexane | 14.9 | 14.9 | 0.0 |
| Iodomethane | 20.9 | 20.1 | 5.7 |
| Methylcyclohexane | 16.0 | 16.0 | 0.0 |
| Methyl ethyl ketone | 19.3 | 15.9 | 11.0 |
| Nitromethane | 26.4 | 16.7 | 20.5 |
| Styrene | 19.1 | 18.7 | 4.1 |
| Tetrachloromethane | 17.5 | 17.5 | 0.0 |
| Tetrahydrofuran | 19.5 | 16.8 | 9.8 |
| Toluene | 18.3 | 18.1 | 2.7 |
| Trichloroethylene | 18.7 | 18.2 | 4.6 |
| Trichloromethane | 18.7 | 17.1 | 6.2 |
| 1,1,1-Trichloroethane | 17.5 | 16.9 | 4.8 |
| <i>p</i> -Xylene | 18.1 | 18.0 | 0.8 |

Adapted from Dickerson, C. G. and Wiche, I. A., *Pac. Chem. Eng. Congr. (Proc.)*, 2(1), 243, 1977.

1. Evaluation of the total cohesion parameter or Hildebrand parameter δ_i as outlined in Section 7.2.
2. Separation of the total cohesion parameter by calculation of the aggregation number (α) from a regression analysis of molar volumes as a function of ratio of boiling point to critical temperature as well as molecular weight, and density

$$\log \alpha = 3.39066 T_b/T_c - 0.15848 - \log (M/\rho) \quad (71)$$

The ratio T_b/T_c may be estimated from Lydersen's equation,

$$(T_b/T_c = 0.567 + \sum_i \Delta_T - (\sum_i \Delta_T)^2) \quad (72)$$

and the Δ_T values (critical temperature Lydersen group constants) were provided by Hoy,¹²⁵ also (Table 17), so it is possible to estimate the component cohesion parameters

TABLE 17
Lydersen Group Constants

| Group, z | $10^2 \Delta_T$ | | $10^2 \Delta_T^P$ |
|-------------------------|-----------------|--------|-------------------|
| | Aliphatic | Cyclic | |
| -CH ₃ | 2.0 | — | 2.26 |
| -CH ₂ - | 2.0 | 1.3 | 2.00 |
| >CH- | 1.2 | 1.2 | 1.31 |
| >C< | 0.0 | -0.7 | 0.40 |
| =CH ₂ | 1.8 | — | 1.92 |
| =CH- | 1.8 | 1.1 | 1.84 |
| =C< | 0.0 | 1.1 | 1.29 |
| =CH- (aromatic) | — | 1.1 | 1.78 |
| =C (aromatic) | — | 1.1 | 1.49 |
| -O- | 2.1 | 1.4 | 1.75 |
| >O (epoxide) | — | 2.7 | 2.67 |
| -COO- | 4.7 | — | 4.97 |
| >C=O | 4.0 | 3.3 | 4.00 |
| -CHO | 4.8 | — | 4.45 |
| -(CO ₂ O) | 8.6 | — | 8.63 |
| -COOH | 3.9 | — | 3.90 |
| -OH→ | 8.2 | — | 3.43 |
| -OH (primary) | 8.2 | — | 4.93 |
| -OH (secondary) | 8.2 | — | 4.40 |
| -OH (tertiary) | 8.2 | — | 5.93 |
| -OH (phenolic) | 3.5 | — | 6.00 |
| -NH ₂ | 3.1 | — | 3.45 |
| -NH- | 3.1 | 2.4 | 2.74 |
| >N- | 1.4 | 0.7 | 0.93 |
| -C=N | 0.6 | — | 5.39 |
| -NCO | 5.4 | — | 5.39 |
| HCON< | 6.2 | — | 5.46 |
| -CONH- | 7.1 | — | 8.43 |
| -CON< | 5.4 | — | 7.29 |
| -CONH ₂ | 7.1 | — | 8.97 |
| -CONH- | 7.8 | — | 9.38 |
| -S- | 1.5 | 0.8 | 3.18 |
| -SH | 1.5 | — | 1.5 |
| -Cl (primary) | 1.7 | — | 3.11 |
| -Cl (secondary) | 1.7 | — | 3.17 |
| -Cl ₂ (twin) | 3.4 | — | 5.21 |
| -Cl (aromatic) | 1.7 | — | 2.45 |
| -Br | 1.0 | — | 3.92 |
| -Br (aromatic) | 1.0 | — | 3.13 |
| -F | 1.8 | — | 0.6 |
| -I | 1.2 | — | — |
| Conjugation | — | — | 0.5 |
| Cis double bond | — | — | -0.10 |
| Trans double bond | — | — | -0.20 |
| 4-membered ring | — | — | 1.18 |
| 5-membered ring | — | — | 0.3 |
| 6-membered ring | — | — | -0.35 |
| 7-membered ring | — | — | 0.69 |

TABLE 17 (continued)
Lyderson Group Constants

| Group, z | $10^2 \cdot \Delta_r$ | | $10^2 \cdot \Delta_r^2$ |
|----------------|-----------------------|--------|-------------------------|
| | Aliphatic | Cyclic | |
| Ortho | — | — | 0.15 |
| Meta | — | — | 0.10 |
| Para | — | — | 0.60 |
| Bicycloheptyl | — | — | 0.34 |
| Tricyclodecane | — | — | 0.95 |

Adapted from Hoy, K. L., *The Hoy Tables of Solubility Parameters*, Union Carbide Corporation, Solvents and Coatings Materials Division, South Charleston, WV, 1985.

knowing only the density and structure, although the accuracy is limited by the approximations made.

3. Calculation of the hydrogen-bonding parameter from

$$\delta_h = \delta_t [(\alpha - 1)/\alpha]^{1/2} \quad (73)$$

4. Evaluation of the polar parameter by a group molar attraction method based on Equation 34, Chapter 6, with the data of Table 7, Chapter 6:

$$\delta_p = \delta_t [\sum_z^2 F_p / (\alpha \sum_z^2 F)]^{1/2} \quad (74)$$

5. Calculation of the nonpolar parameter δ_d by difference (Equation 65).

Hoy's values of δ_t , δ_d , δ_p , and δ_h are included in Table 18. Estimates of three-component parameters for phenol, resorcinol, and about 50 alkyl derivatives have been published by Lille, Kundel, and Eisen¹³⁸ (Table 19). Stekol'shchikov, Krivtsova, and Ratner¹³⁹ have calculated values for hydrocarbons and a few other liquids (Table 20) by various semi-empirical methods based on correlations with physical properties (Section 8.2), and have compared them with literature data. Martin, Wu, and Beerbower^{140,141} used three-component cohesion parameters in their study of solubilities of solids in polar and nonpolar liquids (Section 12.2).

Hoy's dispersion components, δ_d , being evaluated by difference, may be considered less reliable than those of Hansen, which were evaluated directly by homomorph methods. On the other hand, Hansen's method introduces small hydrogen-bonding components to the aromatic liquids. The positron method for evaluation of multicomponent cohesion parameters for liquids, mentioned in Section 3.6, may be able to provide more correct separations of the components. The positronium (Ps) state in pure liquids is considered a "bubble" state as a result of strong repulsive interactions with liquid molecules at short distances. It has been suggested by Mogensen¹⁴² that hydrogen bonds in the liquid are not broken when the Ps bubble is formed, so most of the molecules in its vicinity continue to participate in hydrogen bonding to the same extent as in the bulk liquid. Consequently, the Ps "pick off" rates should be able to be used to determine either δ_d or $(\delta_d^2 + \delta_p^2)^{1/2}$, permitting evaluation of δ_h by optimization of solubility behavior. The positron method seems to show correct component values; correlation with the Hansen δ_d values is better than with the Hoy δ_d results, whereas the $(\delta_d^2 + \delta_p^2)^{1/2}$ correlation is better with the Hoy data than with the Hansen figures, and the hydrogen-bonding components in Hansen's values for aromatic liquids are not supported.

TABLE 18
Hoy's Cohesion Parameters for Liquids (and Solids as Subcooled Liquids) at 25°C

| Liquid | M/g mol ⁻¹ | ρ/g cm ⁻³ | δ/MPa ^{1/2} | | | |
|--|-----------------------|----------------------|----------------------|----------------|----------------|----------------|
| | | | δ _a | δ _p | δ _b | δ _t |
| Acetaldehyde | 44.1 | 0.771 | 11.5 | 10.6 | 12.7 | 20.2 |
| Acetic acid, ethanoic acid | 60.1 | 1.044 | 13.9 | 12.2 | 18.9 | 26.5 |
| Acetic anhydride | 102.1 | 1.075 | 10.0 | 11.3 | 15.7 | 21.8 |
| Acetone, 2-propanone | 58.1 | 0.785 | 13.0 | 9.8 | 11.0 | 19.7 |
| Acetonitrile | 41.1 | 0.776 | 10.3 | 11.1 | 19.6 | 24.8 |
| Acetophenone, 1-phenylethanone | 120.2 | 1.024 | 16.1 | 11.9 | 8.2 | 21.6 |
| 1-Acetoxy-1,3-butadiene | 112.1 | 0.947 | 14.2 | 9.9 | 8.7 | 19.4 |
| Acetylacetone, 2,4-pentanedione | 100.1 | 0.968 | 11.3 | 11.8 | 10.7 | 19.5 |
| Acrolein, 2-propenal | 56.1 | 0.835 | 11.4 | 11.1 | 12.2 | 20.1 |
| Acrylic acid, 2-propenoic acid | 72.1 | 1.040 | 13.5 | 12.8 | 17.9 | 25.9 |
| Acrylonitrile, 2-propenenitrile | 53.1 | 0.801 | 10.6 | 12.5 | 14.0 | 21.6 |
| Allyl acetate | 100.1 | 0.922 | 14.0 | 9.5 | 8.3 | 18.8 |
| Allyl acetoacetate | 142.2 | 1.032 | 13.4 | 11.3 | 10.5 | 20.5 |
| Allyl alcohol, 2-propen-1-ol | 58.1 | 0.848 | 13.0 | 11.8 | 18.7 | 25.7 |
| Allyl chloride, 3-chloropropene | 76.5 | 0.931 | 13.8 | 8.9 | 7.3 | 18.0 |
| Allyl cyanide, 3-butenenitrile | 67.1 | 0.830 | 12.3 | 11.8 | 13.2 | 21.6 |
| <i>N</i> -(2-Aminoethyl)ethanolamine | 104.2 | 1.025 | 13.9 | 12.8 | 20.8 | 28.1 |
| <i>N</i> -(2-Aminoethyl)piperazine | 129.2 | 0.978 | 15.6 | 11.7 | 9.0 | 21.4 |
| <i>N</i> -(3-Aminopropyl)morpholine | 144.2 | 0.981 | 16.1 | 10.2 | 7.3 | 20.4 |
| Amyl alcohol, see 1-Pentanol | | | | | | |
| <i>sec</i> -Amyl alcohol, see 2-Pentanol | 88.2 | 0.815 | 14.5 | 9.1 | 13.9 | 22.0 |
| <i>prim. active</i> Amyl alcohol, 2-methyl-1-butanol | | | | | | |
| <i>tert</i> -Amyl alcohol, 2-methyl-2-butanol | 88.2 | 0.805 | 13.8 | 10.0 | 12.4 | 21.1 |
| Benzene | 78.1 | 0.874 | 16.1 | 8.6 | 4.1 | 18.7 |
| Benzyl alcohol, benzenemethanol | 108.1 | 1.042 | 14.7 | 12.2 | 15.6 | 24.6 |
| Benzyl Cellosolve® | 152.2 | 1.064 | 14.2 | 10.2 | 13.8 | 22.3 |
| <i>N,N</i> -(Bis(3-aminopropyl))methylamine | 145.3 | 0.897 | 14.3 | 9.9 | 10.1 | 20.1 |
| Bromobenzene | 157.0 | 1.486 | 18.4 | 8.2 | 0.0 | 20.1 |
| 2-Bromobutane, <i>sec</i> -butyl bromide | 137.0 | 1.251 | 16.9 | 4.4 | 3.0 | 17.7 |
| Bromochloromethane | 129.4 | 1.919 | 16.9 | 11.1 | 6.5 | 21.2 |
| Bromoethane, ethyl bromide | 109.0 | 1.447 | 16.2 | 5.1 | 6.6 | 18.2 |
| <i>o</i> -Bromostyrene | 183.1 | 1.408 | 17.7 | 9.6 | 0.0 | 20.1 |
| <i>o</i> -Bromotoluene | 171.0 | 1.437 | 17.9 | 8.8 | 0.0 | 20.0 |
| <i>p</i> -Bromotoluene | 171.0 | 1.391 | 17.7 | 8.4 | 0.0 | 19.6 |
| Bromotrichloromethane | 198.3 | 1.998 | 12.0 | 13.8 | 3.1 | 18.6 |
| 1,3-Butadiene | 54.1 | 0.614 | 13.0 | 6.3 | 4.5 | 15.1 |
| Butadiene dioxide | 86.1 | 1.106 | 16.5 | 13.1 | 11.6 | 24.1 |
| Butane | 58.1 | 0.572 | 13.5 | 0.0 | 0.0 | 13.5 |
| 1,4-Butanediol | 90.1 | 1.013 | 15.0 | 13.6 | 27.0 | 33.7 |
| 1-Butanol, butyl alcohol | 74.1 | 0.806 | 15.0 | 10.0 | 15.4 | 23.7 |
| 2-Butanol, <i>sec</i> -butyl alcohol | 74.1 | 0.802 | 14.5 | 9.1 | 14.8 | 22.7 |
| 1-Butene | 56.1 | 0.588 | 12.7 | 4.2 | 2.9 | 13.6 |
| <i>cis</i> -2-Butene | 56.1 | 0.614 | 12.9 | 3.8 | 5.8 | 14.6 |
| <i>trans</i> -2-Butene | 56.1 | 0.597 | 13.1 | 3.6 | 4.2 | 14.2 |
| <i>cis</i> -1-Butenyl methyl ether | 86.1 | 0.770 | 14.2 | 6.4 | 6.2 | 16.8 |
| <i>trans</i> -2-Butenyl methyl ether | 86.1 | 0.780 | 13.9 | 6.2 | 6.4 | 16.5 |
| 3-Butoxybutanol | 146.2 | 0.879 | 14.2 | 7.4 | 11.7 | 19.9 |
| Butoxydipropylene glycol | 190.3 | 0.911 | 14.5 | 8.2 | 7.0 | 18.1 |
| Butoxyethoxypropanol | 176.3 | 0.925 | 13.6 | 7.8 | 11.6 | 19.6 |
| Butyl acetate | 116.2 | 0.876 | 14.5 | 7.8 | 6.8 | 17.8 |
| <i>sec</i> -Butyl acetate | 116.2 | 0.867 | 13.7 | 7.7 | 5.0 | 16.5 |
| Butyl acetoacetate | 158.2 | 0.963 | 13.6 | 9.5 | 10.3 | 19.5 |
| Butyl acrylate | 128.2 | 0.895 | 14.0 | 8.3 | 6.8 | 17.7 |
| Butylamine | 73.1 | 0.734 | 13.6 | 8.1 | 8.0 | 17.7 |

TABLE 18 (continued)
 Hoy's Cohesion Parameters for Liquids (and Solids as Subcooled Liquids) at 25°C

| Liquid | M/g mol ⁻¹ | $\rho/g\text{ cm}^{-3}$ | $\delta/\text{MPa}^{1/2}$ | | | |
|--|-----------------------|-------------------------|---------------------------|------------|------------|------------|
| | | | δ_d | δ_p | δ_h | δ_t |
| Butylaniline | 149.2 | 0.923 | 16.9 | 9.1 | 6.6 | 20.4 |
| Butylbenzene | 134.2 | 0.855 | 16.3 | 6.5 | 0.0 | 17.5 |
| Butyl benzoate | 178.2 | 1.001 | 15.9 | 9.4 | 5.9 | 19.4 |
| Butyl butyrate | 144.2 | 0.865 | 14.6 | 6.9 | 6.2 | 17.3 |
| Butyl Carbitol® | 162.2 | 0.948 | 13.3 | 8.1 | 12.6 | 20.0 |
| Butyl Carbitol acetate | 204.3 | 0.974 | 14.2 | 8.1 | 8.7 | 18.5 |
| Butyl Cellosolve® | 118.2 | 0.896 | 13.3 | 7.9 | 13.0 | 20.2 |
| Butyl Cellosolve® acetate | 160.2 | 0.936 | 14.4 | 8.0 | 7.8 | 18.2 |
| Butyl chloride, see chlorobutane | | | | | | |
| Butyl cyclohexane | 140.3 | 0.794 | 16.1 | 2.4 | 0.0 | 16.2 |
| Butylcyclohexylamine | 155.3 | 0.839 | 16.0 | 6.3 | 3.0 | 17.4 |
| Butylcyclopentane | 126.2 | 0.779 | 16.1 | 2.9 | 0.0 | 16.4 |
| Butylene glycol, butanediol | 90.1 | 1.001 | 12.3 | 12.2 | 22.2 | 28.1 |
| Butylene oxide | 72.1 | 0.824 | 15.0 | 8.0 | 7.0 | 18.4 |
| Butylethanolamine | 117.2 | 0.888 | 14.4 | 9.1 | 15.0 | 22.7 |
| Butyl ether, 1,1'-oxybisbutane | 130.2 | 0.764 | 14.6 | 4.3 | 4.5 | 15.9 |
| Butyl ethyl Cellosolve® | 146.2 | 0.833 | 14.4 | 6.0 | 6.2 | 16.8 |
| Butyl isopropenyl ether | 114.2 | 0.784 | 15.2 | 6.2 | 1.8 | 16.5 |
| Butyl lactate | 146.2 | 0.972 | 12.5 | 9.6 | 12.3 | 20.0 |
| Butyl methyl Cellosolve® | 132.2 | 0.841 | 14.6 | 6.3 | 6.7 | 17.2 |
| Butyl- α -methylbenzylamine | 177.3 | 0.890 | 15.3 | 7.9 | 4.1 | 17.7 |
| Butyl 6-methyl-3-cyclohexane carboxylate | 196.3 | 0.939 | 15.4 | 7.5 | 2.2 | 17.3 |
| 2-Butyloctanol | 186.3 | 0.831 | 14.5 | 6.3 | 10.0 | 18.8 |
| Butyl salicylate | 194.2 | 1.069 | 15.6 | 11.2 | 5.4 | 19.9 |
| <i>o</i> -Butyltoluene | 148.2 | 0.865 | 16.6 | 6.1 | 0.0 | 17.7 |
| <i>m</i> -Butyltoluene | 148.2 | 0.853 | 16.5 | 6.0 | 0.0 | 17.5 |
| <i>p</i> -Butyltoluene | 148.2 | 0.851 | 16.5 | 5.9 | 0.0 | 17.5 |
| Butyraldehyde, butanal | 72.1 | 0.796 | 13.1 | 8.9 | 9.6 | 18.6 |
| Butyric acid, butanoic acid | 88.1 | 0.953 | 15.8 | 10.2 | 15.8 | 24.5 |
| Butyric anhydride | 158.2 | 0.962 | 13.1 | 10.2 | 8.9 | 18.8 |
| γ -Butyrolactone | 86.1 | 1.122 | 18.6 | 12.2 | 14.0 | 26.3 |
| Butyronitrile | 69.1 | 0.786 | 13.3 | 10.6 | 12.0 | 20.8 |
| ϵ -Caprolactone | 114.1 | 1.071 | 19.1 | 9.9 | 14.4 | 25.9 |
| Carbitol® acetate | 176.2 | 1.004 | 14.4 | 9.0 | 9.4 | 19.4 |
| Carbitol | 134.2 | 0.983 | 13.0 | 8.9 | 14.1 | 21.2 |
| Carbon disulfide | 76.1 | 1.256 | 10.9 | 16.6 | 4.3 | 20.3 |
| Cellosolve® acetate | 132.2 | 0.968 | 14.4 | 9.0 | 8.9 | 19.1 |
| Cellosolve acrylate | 144.2 | 0.976 | 14.2 | 9.4 | 8.7 | 19.1 |
| Cellosolve | 90.1 | 0.925 | 13.0 | 9.1 | 15.2 | 21.9 |
| 2-Chloroallylidene diacetate | 192.6 | 1.202 | 14.9 | 11.8 | 7.5 | 20.4 |
| Chlorobenzene | 112.6 | 1.098 | 17.4 | 9.4 | 0.0 | 19.7 |
| 2-Chloro-1,3-butadiene | 88.5 | 0.949 | 15.0 | 7.5 | 3.5 | 17.2 |
| 1-Chlorobutane, butyl chloride | 92.6 | 0.880 | 15.3 | 6.9 | 3.5 | 17.1 |
| 2-Chlorobutane, <i>sec</i> -butyl chloride | 92.6 | 0.867 | 14.9 | 6.9 | 2.4 | 16.6 |
| 2-Chloroethyl acetate | 122.6 | 1.140 | 15.1 | 11.4 | 9.6 | 21.2 |
| 2-Chloroethyl ethyl ether | 108.6 | 0.992 | 14.4 | 8.5 | 7.5 | 18.4 |
| Chloroform, see trichloromethane | | | | | | |
| 1-Chloropropane, propyl chloride | 78.5 | 0.885 | 14.4 | 7.2 | 6.0 | 17.2 |
| 2-Chloropropane, isopropyl chloride | 78.5 | 0.856 | 14.2 | 7.3 | 4.3 | 16.5 |
| <i>o</i> -Chlorostyrene | 138.6 | 1.093 | 17.1 | 9.4 | 0.0 | 19.6 |
| <i>p</i> -Chlorostyrene | 138.6 | 1.080 | 17.2 | 9.2 | 0.0 | 19.5 |
| Crotonaldehyde, 2-butenal | 70.1 | 0.847 | 13.4 | 10.5 | 11.5 | 20.5 |
| Cyclohexane | 84.2 | 0.774 | 16.5 | 3.1 | 0.0 | 16.8 |
| Cyclohexanol, cyclohexyl alcohol | 100.1 | 0.956 | 13.8 | 8.6 | 15.3 | 22.3 |
| Cyclohexanone | 98.2 | 0.942 | 15.6 | 9.4 | 11.0 | 21.3 |

TABLE 18 (continued)
Hoy's Cohesion Parameters for Liquids (and Solids as Subcooled Liquids) at 25°C

| Liquid | M/g mol ⁻¹ | $\rho/g\text{ cm}^{-3}$ | $\delta/\text{MPa}^{1/2}$ | | | |
|---|-----------------------|-------------------------|---------------------------|------------|------------|------------|
| | | | δ_d | δ_p | δ_h | δ_t |
| 1-Cyclohexyldecane | 224.4 | 0.814 | 15.9 | 1.9 | 0.0 | 16.1 |
| 1-Cyclohexyldecane | 252.5 | 0.818 | 15.9 | 1.8 | 0.0 | 16.0 |
| 1-Cyclohexylheptane | 182.3 | 0.806 | 16.0 | 2.1 | 0.0 | 16.1 |
| 1-Cyclohexylnonane | 210.4 | 0.811 | 16.0 | 1.9 | 0.0 | 16.1 |
| 1-Cyclohexyloctane | 196.4 | 0.809 | 16.0 | 2.0 | 0.0 | 16.1 |
| 1-Cyclohexylundecane | 238.4 | 0.815 | 15.9 | 1.8 | 0.0 | 16.0 |
| Cyclopentane | 70.1 | 0.739 | 16.1 | 3.9 | 0.6 | 16.5 |
| Cyclopentanone | 84.1 | 0.944 | 16.2 | 11.1 | 8.8 | 21.5 |
| Cyclopentene | 68.1 | 0.765 | 15.3 | 5.8 | 4.1 | 16.9 |
| 2-Cyclopentenyl alcohol | 84.1 | 0.976 | 15.4 | 11.5 | 16.5 | 25.3 |
| 1-Cyclopentyldecane | 210.4 | 0.806 | 17.2 | 2.4 | 1.3 | 17.4 |
| 1-Cyclopentylheptane | 168.3 | 0.796 | 16.6 | 2.6 | 0.0 | 16.8 |
| 1-Cyclopentylhexane | 154.3 | 0.791 | 16.5 | 2.7 | 0.0 | 16.7 |
| 1-Cyclopentylnonane | 196.4 | 0.803 | 17.0 | 2.4 | 0.0 | 17.1 |
| 1-Cyclopentylloctane | 182.3 | 0.800 | 16.7 | 2.5 | 0.0 | 16.9 |
| 1-Cyclopentylpentane | 140.3 | 0.786 | 16.2 | 2.8 | 0.0 | 16.5 |
| 1-Cyclopentylundecane | 224.4 | 0.808 | 17.2 | 2.3 | 1.2 | 17.4 |
| Decane | 142.3 | 0.725 | 15.8 | 0.0 | 0.0 | 15.8 |
| 1-Decanol, decyl alcohol | 158.3 | 0.826 | 15.4 | 7.0 | 11.6 | 20.5 |
| 2-Decanol, <i>sec</i> -decyl alcohol | 158.3 | 0.821 | 13.8 | 6.2 | 9.8 | 18.0 |
| 1-Decene | 140.3 | 0.736 | 15.7 | 3.3 | 1.3 | 16.0 |
| Decylbenzene | 218.4 | 0.850 | 16.5 | 5.0 | 0.0 | 17.3 |
| Diacetone alcohol | 116.2 | 0.934 | 10.7 | 11.4 | 12.6 | 20.0 |
| Diallylamine | 97.2 | 0.783 | 13.5 | 8.5 | 7.5 | 17.6 |
| 1,1-Diallyloxyethane | 142.2 | 0.871 | 13.3 | 8.0 | 6.2 | 16.7 |
| 3,3'-Diaminodipropylamine | 131.2 | 0.925 | 13.7 | 11.5 | 12.9 | 22.1 |
| 1,3-Diaminopropane | 74.1 | 0.882 | 13.9 | 12.9 | 14.7 | 24.0 |
| <i>o</i> -Dibromobenzene | 235.9 | 1.973 | 18.5 | 10.0 | 0.0 | 21.0 |
| Dibutylamine | 129.3 | 0.757 | 14.6 | 5.6 | 5.7 | 16.7 |
| Dibutyl Carbitol® | 218.3 | 0.880 | 14.3 | 6.1 | 7.1 | 17.0 |
| Dibutyl Cellosolve® | 174.3 | 0.832 | 14.6 | 5.5 | 6.1 | 16.8 |
| <i>N,N</i> -Dibutylethanolamine | 173.3 | 0.856 | 13.2 | 6.0 | 9.9 | 17.6 |
| Dibutyl fumarate | 228.3 | 0.981 | 14.2 | 8.6 | 8.0 | 18.4 |
| Dibutylisopropanolamine | 187.3 | 0.837 | 13.2 | 5.8 | 8.8 | 16.9 |
| Dibutyl maleate | 228.3 | 0.990 | 14.1 | 8.6 | 8.4 | 18.5 |
| Dibutyl phthalate | 278.4 | 1.042 | 15.9 | 9.5 | 8.1 | 20.2 |
| <i>o</i> -Dichlorobenzene | 147.0 | 0.298 | 18.0 | 9.8 | 0.0 | 20.5 |
| <i>m</i> -Dichlorobenzene | 147.0 | 0.281 | 17.6 | 9.5 | 0.0 | 20.0 |
| <i>p</i> -Dichlorobenzene | 147.0 | 0.239 | 17.5 | 9.2 | 0.0 | 19.8 |
| 1,1-Dichloroethane, ethylidene chloride | 99.0 | 1.168 | 13.8 | 10.5 | 5.6 | 18.3 |
| 1,2-Dichloroethane, ethylene dichloride | 99.0 | 1.246 | 14.2 | 11.2 | 9.1 | 20.2 |
| Di(2-Chloroethoxy)methane | 173.0 | 1.226 | 13.4 | 10.2 | 12.6 | 21.1 |
| Di(2-Chloroethyl) ether | 143.0 | 1.214 | 15.4 | 11.0 | 9.1 | 21.0 |
| Dichloroisopropyl ether | 171.1 | 1.106 | 15.2 | 9.7 | 4.6 | 18.6 |
| Dichloromethane, methylene dichloride | 84.9 | 1.316 | 13.4 | 11.7 | 9.6 | 20.2 |
| 1,3-Dichloropropane, propylene dichloride | 113.0 | 1.150 | 14.4 | 10.4 | 5.4 | 18.5 |
| 2,3-Dichloropropanol | 129.0 | 1.355 | 12.2 | 13.6 | 16.4 | 24.6 |
| Dicrotylpropional | 184.3 | 0.870 | 14.6 | 7.1 | 6.6 | 17.5 |
| Di(1,3-dimethylbutyl)amine | 185.4 | 0.781 | 14.4 | 4.9 | 1.5 | 15.3 |
| 1,1-Diethoxybutane | 146.2 | 0.823 | 13.8 | 6.2 | 4.9 | 15.9 |
| 1,1-Diethoxyethane | 118.2 | 0.821 | 13.5 | 6.8 | 5.1 | 15.9 |
| 2,5-Diethoxytetrahydrofuran | 161.2 | 0.962 | 14.4 | 7.7 | 5.9 | 17.3 |
| Diethoxytriglycol | 206.3 | 0.950 | 14.2 | 7.5 | 8.8 | 18.3 |
| Diethylamine | 73.1 | 0.701 | 13.4 | 7.0 | 6.3 | 16.5 |

TABLE 18 (continued)
Hoy's Cohesion Parameters for Liquids (and Solids as Subcooled Liquids) at 25°C

| Liquid | M/g mol ⁻¹ | $\rho/\text{g cm}^{-3}$ | $\delta/\text{MPa}^{1/2}$ | | | |
|---------------------------------------|-----------------------|-------------------------|---------------------------|------------|------------|------------|
| | | | δ_d | δ_p | δ_h | δ_t |
| Diethylaminoethylamine | 116.2 | 0.815 | 14.0 | 7.8 | 7.1 | 17.5 |
| 3-(Diethylamino)propylamine | 130.2 | 0.823 | 14.4 | 7.4 | 7.1 | 17.7 |
| 1,2-Diethylbenzene | 134.2 | 0.874 | 16.6 | 6.5 | 0.0 | 17.8 |
| 1,3-Diethylbenzene | 134.2 | 0.858 | 16.6 | 6.3 | 0.0 | 17.7 |
| 1,4-Diethylbenzene | 134.2 | 0.856 | 16.6 | 6.2 | 0.0 | 17.7 |
| Diethyl Carbitol® | 162.2 | 0.902 | 14.1 | 7.1 | 8.0 | 17.7 |
| Diethyl Cellosolve® | 118.2 | 0.835 | 14.3 | 6.7 | 6.7 | 17.1 |
| Diethylene glycol, 2,2'-oxybisethanol | 106.1 | 1.113 | 12.4 | 12.3 | 23.3 | 29.1 |
| Diethylenetriamine | 103.2 | 0.948 | 13.0 | 13.1 | 14.7 | 23.6 |
| N,N-Diethylethanolamine | 117.2 | 0.879 | 13.1 | 7.3 | 12.0 | 19.2 |
| Diethyl 2-ethylhexanal | 202.3 | 0.835 | 14.2 | 5.3 | 4.9 | 16.0 |
| Diethyl 2-ethyl-3-methylglutarate | 230.2 | 0.976 | 13.6 | 8.0 | 6.7 | 17.1 |
| Diethyl fumarate | 172.2 | 1.046 | 13.8 | 10.3 | 9.3 | 19.5 |
| 3,3-Diethylhexane | 142.3 | 0.762 | 15.7 | 0.0 | 0.0 | 15.7 |
| 3,4-Diethylhexane | 142.3 | 0.749 | 15.4 | 0.0 | 0.0 | 15.4 |
| Di(3-ethylhexyl)amine | 241.5 | 0.801 | 14.6 | 4.2 | 4.8 | 16.0 |
| Di(2-ethylhexyl) ether | 242.5 | 0.807 | 14.9 | 3.3 | 4.2 | 15.9 |
| Diethylisopropanolamine | 131.2 | 0.841 | 12.4 | 6.7 | 9.7 | 17.1 |
| Diethyl ketone, 3-pentanone | 86.1 | 0.809 | 14.5 | 8.7 | 7.6 | 18.5 |
| Diethyl maleate | 172.2 | 1.063 | 14.3 | 10.5 | 9.9 | 20.3 |
| 3,3-Diethylpentane | 128.3 | 0.749 | 15.4 | 0.0 | 0.0 | 15.4 |
| 2,2-Diethylpentanol | 144.3 | 0.853 | 14.2 | 7.3 | 10.6 | 19.2 |
| Diethyl phthalate | 222.3 | 1.114 | 15.0 | 10.9 | 8.5 | 20.4 |
| Diethyl pimelate | 216.3 | 0.988 | 14.4 | 8.5 | 8.3 | 18.6 |
| Diethyl succinate | 172.2 | 1.035 | 14.3 | 9.8 | 9.4 | 19.7 |
| 3,9-Diethyl-6-tridecanol | 256.5 | 0.843 | 14.4 | 5.2 | 7.5 | 17.0 |
| Diglycolamine | 105.1 | 1.051 | 11.9 | 11.1 | 19.2 | 25.1 |
| Diglycol chlorohydrin | 124.6 | 1.168 | 13.3 | 12.1 | 17.1 | 24.8 |
| Diglycol diacetate | 190.2 | 1.108 | 14.7 | 10.7 | 11.2 | 21.3 |
| Dihexylamine | 185.4 | 0.785 | 15.1 | 4.8 | 6.1 | 17.0 |
| Dihexyl ether | 186.4 | 0.789 | 15.1 | 3.7 | 5.2 | 16.4 |
| 1,1-Diisobutoxyethane | 174.3 | 0.815 | 14.2 | 5.8 | 2.6 | 15.6 |
| Diisobutylene | 112.2 | 0.711 | 13.9 | 3.4 | 0.0 | 14.3 |
| Diisobutyl ketone | 142.2 | 0.802 | 14.5 | 6.8 | 3.9 | 16.5 |
| 1,1-Diisopropoxyethane | 146.2 | 0.810 | 13.6 | 6.2 | 1.7 | 15.1 |
| Diisopropylamine | 101.2 | 0.712 | 13.8 | 6.2 | 2.0 | 15.2 |
| Diisopropylethanolamine | 145.3 | 0.870 | 14.1 | 6.9 | 10.5 | 18.9 |
| Diisopropyl maleate | 200.2 | 1.005 | 14.4 | 9.6 | 7.2 | 18.7 |
| Diketene | 84.1 | 1.108 | 14.5 | 13.5 | 12.7 | 23.6 |
| 1,3-Dimethoxybutane | 118.2 | 0.844 | 14.2 | 6.7 | 6.0 | 16.9 |
| 1,1-Dimethoxyethane | 90.1 | 0.845 | 13.0 | 7.8 | 6.8 | 16.6 |
| 1,1-Di(methoxyethoxy)ethane | 178.2 | 0.971 | 13.8 | 8.4 | 8.8 | 18.4 |
| 1,1-Di(methoxyethoxy)methane | 164.2 | 0.991 | 14.0 | 8.8 | 10.0 | 19.3 |
| 1,1-Dimethoxy-2-methylpropane | 118.2 | 0.839 | 13.5 | 7.0 | 4.7 | 15.9 |
| Dimethoxytetraglycol | 222.3 | 1.007 | 14.5 | 8.4 | 10.3 | 19.7 |
| 3-(Dimethylamino)propionitrile | 98.2 | 0.866 | 14.3 | 10.5 | 11.4 | 21.1 |
| 3-(Dimethylamino)propylamine | 102.2 | 0.812 | 14.6 | 8.5 | 7.9 | 18.6 |
| Di(α -methylbenzyl) ether | 226.3 | 0.997 | 16.3 | 8.9 | 0.0 | 18.6 |
| 2,2-Dimethylbutane | 86.2 | 0.643 | 13.7 | 0.0 | 0.0 | 13.7 |
| 2,3-Dimethylbutane | 86.2 | 0.656 | 14.2 | 0.0 | 0.0 | 14.2 |
| 2,2-Dimethylbutanol | 102.2 | 0.824 | 14.6 | 8.7 | 12.1 | 20.8 |
| 2,3-Dimethylbutanol | 102.2 | 0.826 | 14.1 | 8.5 | 12.2 | 20.5 |
| 2,4-Dimethylbutanol | 102.2 | 0.809 | 14.2 | 8.5 | 11.4 | 20.1 |
| 2,3-Dimethyl-2-butanol | 102.2 | 0.819 | 13.4 | 9.4 | 10.7 | 19.6 |