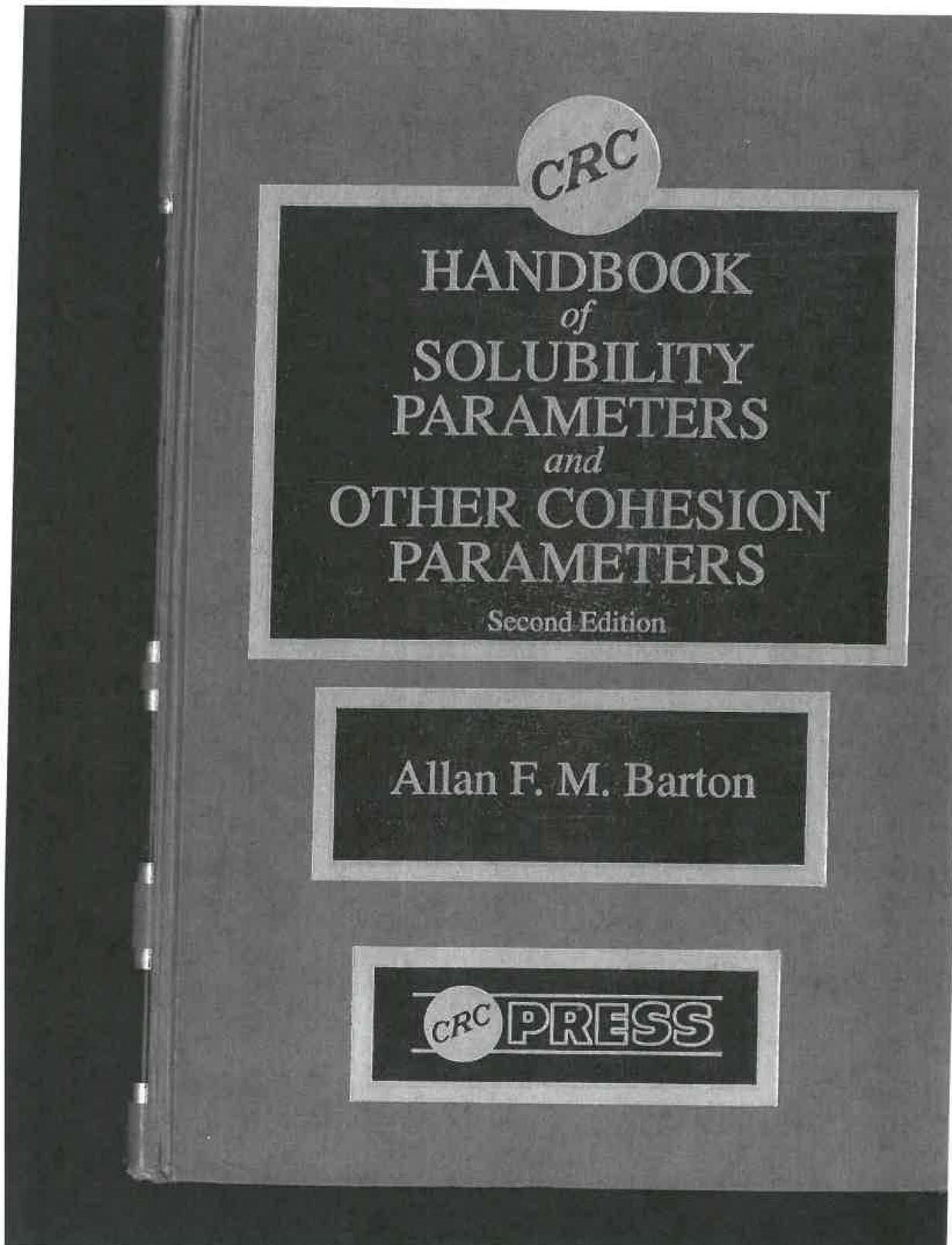
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Allan F. M. Barton
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Chapter 2

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, ${}_{l}\Delta_{g}U$, 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

$$-U = {}_{l}\Delta_{g}U + {}_{g}\Delta_{\infty}\mathrm{U} = {}_{l}\Delta_{g}\mathrm{u} + \int_{V={}^{g}V}^{V=\infty} (\partial U/\partial V)_{T}\, \mathrm{d}V \qquad (1)$$

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

$$-U = {}_{l}\Delta_{g} H + {}_{g}\Delta_{\infty}H - RT + p_{s}{}^{l}V \qquad (2)$$

where ${}_{l}\Delta_{g}H$ 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; ${}^{l}V$ 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 J K^{-1} mol^{-1}). At pressures below atmospheric pressure (that is, at temperatures below the normal boiling point) ${}_{g}\Delta_{\infty}H$ and $p_{s}{}^{l}V$ are usually negligible compared with ${}_{l}\Delta_{g}H$ and RT:

$$-U = {}_{l}\Delta_{g} U = {}_{l}\Delta_{g}H - RT \qquad (3)$$

However, at higher pressures the other terms cannot be neglected, and in fact at the critical point ${}_{l}\Delta_{g}H$ 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 ${}_l\Delta_g H$, ${}_l\Delta_g{}^g U$, and $-U$ for various liquids at their normal boiling points in Table 1 illustrates typical variations in these quantities.

Svoboda and co-workers[2-7] 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),

$$c = -U/V \tag{4}$$

Cohesive energy density was the basis of the original definition by Hildebrand and Scott[8-10] of what is now generally called the Hildebrand solubility parameter or *Hildebrand parameter*,

$$\delta = c^{1/2} = (-U/V)^{1/2} \approx ({}_l\Delta_g\, U/V)^{1/2} \tag{5}$$

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:

$$\delta = ({}_l\Delta_g\, H - RT)^{1/2}/V^{1/2} \tag{6}$$

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 Scott[10] and presented here in SI units (see Section 2.5). The vaporization enthalpies are corrected for expansion 'ters

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

Liquid	t_b/°C	$_l\Delta_g H$/kJ mol^{-1}	$_l\Delta_g U$/kJ mol^{-1}	$-U$/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
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
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
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/°C	$_l\Delta_g H$/kJ mol^{-1}	$_l\Delta_g U$/kJ mol^{-1}	$-U$/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
o-Xylene,1,2-dimethylbenzene	144.4	36.7	33.4	33.7
m-Xylene,1,3-dimethylbenzene	139.1	36.2	32.9	33.3
p-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 Druzhina[41] 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	$-U$/kJ mol^{-1}
C_2H_6	Ethane	7.7
C_3H_8	Propane	13.9
C_4H_{10}	Butane	19.2
	Isobutane	17.6
C_5H_{12}	Pentane	24.3
	Isopentane	22.8
	Neopentane	19.9
C_6H_{14}	Hexane	29.3
	Branched hexanes	26—28
C_7H_{16}	Heptane	34.2
	Branched heptanes	30—33
C_8H_{18}	Octane	39.1
	Branched octanes	33—41
C_9H_{20}	Nonane	44.0
	Branched nonanes	36—40
$C_{10}H_{22}$	Decane	48.9
	Branched decanes	45—47
$C_{11}H_{24}$	Undecane	54.0
	Branched undecanes	48—52
$C_{12}H_{26}$	Dodecane	59.0
	2,2,4,6,6-Pentamethylheptane	46.5
$C_{13}H_{28}$	Tridecane	64.0
$C_{14}H_{30}$	Tetradecane	68.8
$C_{15}H_{32}$	Pentadecane	73.6
$C_{16}H_{34}$	Hexadecane	78.9
$C_{17}H_{36}$	Heptadecane	83.5
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
$C_{10}H_{20}$	Cycloalkanes	45
$C_{11}H_{22}$	Pentylcyclohexane	51.4
$C_{12}H_{22}$	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
$C_{10}H_{20}$	1-Decene	48.0
$C_{12}H_{24}$	1-Dodecene	58.3
$C_{16}H_{32}$	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	$-U$/kJ mol^{-1}
C_8H_{12}	4-Vinyl-4-cyclohexene	37.1
	cis,cis-1,5-Cyclooctadiene	40.9
C_9H_{10}	Alkylbenzenes	43—48
	cis-5-Ethylidenebicyclo[2.2.1]-2-heptene	41.7
C_9H_{14}	2,3-Dimethylbicyclo[2.2.1]-2-heptene	39.7
$C_{10}H_{14}$	Alkylbenzenes	45—49
$C_{12}H_{16}$	Cyclohexylbenzene	57.5
C_6F_6	Hexafluorobenzene	33.3
C_6HF_5	Pentafluorobenzene	33.9
$C_6H_4F_2$	Difluorobenzenes	32—34
C_6H_5F	Fluorobenzene	32.2
$C_7H_3F_5$	2,3,4,5,6-Pentafluorotoluene	38.7
$C_7H_5F_3$	(Trifluoromethyl)benzene	35.2
C_7H_7F	4-Fluorotoluene	37.0
C_8F_{18}	Octadecafluorooctane	38.7
$C_8H_{17}F$	1-Fluorooctane	47.2
C_9F_{18}	Octadecafluoropropylcyclohexane	40.6
$C_{10}F_{18}$	Octadecafluorodecahydronaphthalenes	43
$C_{10}F_{20}$	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
$C_2H_2Cl_2$	1,1-Dichloroethylene	24.3
$C_2H_2Cl_4$	1,1,2,2-Tetrachloroethane	43.3
$C_2H_3Cl_3$	1,1,1-Trichloroethane	30.1
	1,1,2-Trichloroethane	37.8
$C_2H_4Cl_2$	1,1-Dichloroethane	28.3
	1,2-Dichloroethane	32.7
$C_3H_6Cl_2$	1,3-Dichloropropane	38.3
C_3H_7Cl	1-Chloropropane	26.1
$C_4H_8Cl_2$	1,2-Dichlorobutane	37.1
	1,4-Dichlorobutane	43.9
C_4H_9Cl	1-Chlorobutane	31.2
	Isobutyl chloride	29.3
	sec-Butyl chloride, 2-chlorobutane	29.2
	tert-Butyl chloride	26.7
$C_5H_{10}Cl_2$	1,2-Dichloropentane	41.4
	1,5-Dichloropentane	48.2
$C_5H_{11}Cl$	Chloropentanes	34—36
C_6H_5Cl	Chlorobenzene	38.5
$C_6H_{12}Cl_2$	1,2-Dichlorohexane	45.7
$C_6H_{13}Cl$	1-Chlorohexane	40.4
$C_7H_{15}Cl$	1-Chloroheptane	45.2
$C_8H_{17}Cl$	1-Chlorooctane	49.9
$C_{12}H_{25}Cl$	1-Chlorododecane	68.7
$C_{16}H_{33}Cl$	1-Chlorohexadecane	89.3
$CHBr_3$	Tribromomethane	43.6
CH_2Br_2	Dibromomethane	34.6
CH_3Br	Bromomethane	20.8
$C_2H_4Br_2$	1,2-Dibromoethane	39.3
C_2H_5Br	Bromoethane	25.8
C_3H_5Br	Allyl bromide	30.4
$C_3H_6Br_2$	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_3H_7Br	Bromopropanes	28—30
$C_4H_8Br_2$	1,4-Dibromobutane	50.6
	1,2-Dibromo-2-methylpropane	40.9
C_4H_9Br	Alkyl bromides	30—34
$C_5H_{11}Br$	1-Bromopentane	38.8
C_6H_5Br	Bromobenzene	42.1
$C_6H_{13}r$	1-Bromohexane	43.4
$C_7H_{15}Br$	1-Bromoheptane	48.1
$C_8H_{17}Br$	1-Bromooctane	53.3
$C_{12}H_{25}Br$	1-Bromododecane	72.3
$C_{16}H_{33}Br$	1-Bromohexadecane	91.9
C_2H_5I	Iodoethane	29.6
C_3H_7I	Iodopropanes	32—34
C_4H_9I	Iodobutanes	33—38
$C_5H_{11}I$	1-Iodopentane	42.8
$C_6H_{13}I$	1-Iodohexane	47.3
$C_2Br_2ClF_3$	1,2-Dibromochlorotrifluoroethane	32.6
$C_2Br_2F_4$	1,2-Dibromotetrafluoroethane	26.1
$C_2Cl_3F_3$	Trichlorotrifluoroethanes	26
$C_2HBrClF_3$	Bromochlorotrifluoroethanes	27—28
C_2H_4BrCl	1-Bromo-2-chloroethane	35.7
$C_3Cl_2F_6$	1,2-Dichlorohexafluoropropane	24.8
$C_3H_2Cl_3F_3$	1,1,1-Trichloro-3,3,3-trifluoropropane	34.3
$C_3H_3Cl_2F_3$	1,1-Dichloro-3,3,3-trifluoropropane	31.7
C_3H_6BrCl	1-Bromo-3-chloropropane	41.6
C_6ClF_5	Chloropentafluorobenzene	38.6
CH_5N	Methylamine	21.4
C_2H_7N	Dimethylamine	23.0
$C_2H_8N_2$	1,2-Ethanediamine, ethylene diamine	42.5
C_3H_9N	Propylamine	29.0
	Isopropylamine	26.2
	Trimethylamine	19.7
$C_3H_{10}N_2$	1,3-Propanediamine	47.7
	N-Methyl-1,2-ethanediamine	42.7
$C_4H_{11}N$	Butylamines	29—33
$C_5H_{13}N$	Propylamines	31—38
C_6H_7N	Aniline	53.4
$C_6H_{13}N$	Cyclohexylamine	41.2
$C_6H_{15}N$	Hexylamines	32—43
C_7H_9N	Benzylamine	57.7
$C_7H_{17}N$	Heptylamines	40—48
$C_8H_{11}N$	*N,N*-Dimethylaniline	50.4
$C_8H_{19}N$	Octylamines	47—50
$C_9H_{21}N$	Tripropylamine	43.7
C_2N_2	Ethanedinitrile	18.4
C_2H_3N	Ethanenitrile, acetonitrile	30.9
C_3H_5N	Propanenitrile, propionotrile	33.7
C_4H_5N	Butenenitriles, allyl cyanide	37—38
	Cyclopropanecarbonitrile	39.5
C_4H_7N	Butanenitriles	35—37
C_5H_7N	Pentenenitriles	41—43
	Cyclobutanecarbonitrile	41.9
C_5H_9N	Pentanenitriles	35—41
C_6H_7N	1-Cyclopentenecarbonitrile	42.5
C_6H_9N	Cyclopentanecarbonitrile	41.0
$C_6H_{11}N$	Hexanenitrile, capronitrile	45.4

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

Formula	Compound	$-U$/kJ mol^{-1}
C_7H_9N	1-Cyclohexenecarbonitrile	51.1
$C_7H_{11}N$	Cyclohexanecarbonitrile	49.4
$C_8H_{15}N$	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
$C_4H_4N_2$	Pyridazine	51.0
	Pyrimidine	47.3
	Pyrrole	42.9
C_4H_9N	Pyrrolidine	35.0
C_5H_5N	Pyridine	37.7
C_6H_7N	Methylpyridines, picoline	40—42
C_7H_9N	Dimethylpyridines	43—48
$C_8H_{11}N$	Trimethylpyridines	48
$C_8H_{16}N_2$	3,3,6,6-Tetramethyl-3,4,5,6-tetrahydropyridazine	47.6
CH_6N_2	Methylhydrazine	38.0
$C_2H_8N_2$	Dimethylhydrazines	33—37
$C_5H_{12}N_2$	1-(Methylazo)butane	33.9
$C_6H_{14}N_2$	Azopropane	37.4
	2-(Isopropylazo)propane	33.4
$C_8H_{18}N_2$	Azobutane	46.8
	2-(*tert*-Butylazo)-2-methylpropane	36.6
$C_{12}H_{26}N_2$	2-(*tert*-Butylazo)-2,4,4-trimethylpentane	51.1
$C_{16}H_{34}N_2$	2,2′-Azo-(2,4,4-trimethylpentane)	64.1
C_2H_6O	Dimethyl ether	16.8
$C_4H_{10}O$	Ethers	25
$C_4H_{10}O_2$	1,2-Dimethoxyethane	34.0
$C_5H_{12}O$	Butyl methyl ethers	28—30
	Ethyl propyl ethers	28—29
$C_5H_{12}O_2$	1-Ethoxy-2-methoxyethane	37.4
	Diethoxymethane	33.3
$C_6H_{12}O$	Butyl vinyl ethers	32—34
$C_6H_{14}O$	Methyl pentyl ethers	33—34
	Butyl ethyl ethers	31—34
	Dipropyl ethers	30—33
$C_6H_{14}O_2$	2-Methoxy-1-propoxyethane	41.2
	Diethoxyethane	40.8
$C_6H_{14}O_3$	Bis(ethoxymethyl)ether	42.2
C_7H_8O	Methyl phenyl ether	44.4
$C_7H_{16}O$	Ethers	32—40
$C_7H_{16}O_2$	Diethers	43—45
$C_7H_{16}O_4$	3,5,7,9-Tetraoxoundecane	51.2
$C_8H_{10}O$	Ethyl phenyl ether	48.6
$C_8H_{18}O$	Ethers	35—44
$C_8H_{18}O_2$	Diethers	48—49
$C_8H_{18}O_3$	Diethylene glycol diethyl ether	55.9
$C_9H_{20}O$	Ethers	42—50
$C_9H_{20}O_2$	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_4O	Methanol	35.4
C_2H_6O	Ethanol	40.0
C_3H_8O	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}
$C_4H_{10}O$	1-Butanol	49.9
	Other butanols	44—48
$C_5H_{10}O$	Cyclopentanol	55.2
$C_5H_{12}O$	1-Pentanol	54.6
	Other pentanols	48—53
$C_6H_{12}O$	Cyclohexanol	59.5
$C_6H_{14}O$	1-Hexanol	59.1
	Other hexanols	52—58
$C_7H_{16}O$	1-Heptanol	64.3
$C_8H_{10}O$	Dimethylphenols	62—80
$C_8H_{18}O$	1-Octanol	68.5
$C_9H_{20}O$	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_2H_4O	Ethanal, acetaldehyde	23.7
C_3H_6O	Propanal	27.5
	2-Propanone, acetone	28.8
C_4H_8O	2-Butanone, methyl ethyl ketone	32.4
C_5H_8O	Cyclopentanone	40.3
	Cyclopropyl methyl ketone	37.0
$C_5H_8O_2$	2,4-Pentanedione	40
$C_5H_{10}O$	Pentanones	34—36
$C_6H_{10}O$	Cyclohexanone	43.4
$C_6H_{12}O$	Hexanones	36—41
$C_7H_{10}O$	Dicyclopropyl ketone	51.2
$C_7H_{14}O$	Heptanones	39—45
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	40.8
$C_9H_{14}O$	2-Hexahydroindanone	54—55
$C_9H_{16}O$	Dimethyl-3,5-heptanediones	53.6
$C_9H_{18}O$	Nonanones	43—54
$C_{10}H_{16}O$	*trans*-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_2O_2	Formic acid	43.8
$C_2H_4O_2$	Acetic acid	49.1
$C_3H_6O_2$	Propionic acid	52.5
$C_4H_8O_2$	Butyric acids	51—56
$C_2H_4O_2$	Methyl formate	26
$C_3H_6O_2$	Esters	30
$C_4H_8O_2$	Esters	33—35
$C_5H_8O_2$	Methyl cyclopropanecarboxylate	38.8
$C_5H_{10}O_2$	Esters	35—37
$C_6H_{10}O_2$	Methyl cyclobutanecarboxylate	42.3
	Ethylene glycol diacetate	59.0
$C_6H_{12}O_2$	Esters	36—41
$C_7H_{14}O_2$	Esters	39—46
$C_8H_8O_2$	Methyl benzoate	53.1
$C_8H_{14}O_4$	Ethylene glycol dipropanoate	65.1
$C_8H_{16}O_2$	Esters	49
$C_9H_{14}O_6$	Triacetin	83.3
$C_9H_{18}O_2$	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	$-U$/kJ mol^{-1}
$C_{10}H_{20}O_2$	Methyl nonanoate	59.5
$C_{11}H_{22}O_2$	Methyl decanoate	64.3
$C_{12}H_{20}O_6$	Tripropionin	88.9
$C_{12}H_{24}O_2$	Methyl undecanoate	69.0
$C_{13}H_{26}O_2$	Methyl dodecanoate	74.7
$C_{14}H_{28}O_2$	Methyl tridecanoate	80.2
$C_{15}H_{26}O_6$	Glcyerol tributyrate	104.6
$C_{15}H_{30}O_2$	Methyl tetradecanoate	84.5
$C_{16}H_{32}O_2$	Methyl pentadecanoate	91.0
C_2H_4O	Oxirane, ethylene oxide	23.0
$C_3H_4O_2$	β-Propiolactone	44.6
C_3H_6O	Methyloxirane, propylene oxide	25.8
	Oxetane, trimethylene oxide	27.7
C_4H_4O	Furan	25.2
$C_4H_4O_2$	Diketene	40.4
C_4H_8O	Tetrahydropyran	29.7
$C_4H_8O_2$	1,3-Dioxane	36.7
	1,4-Dioxane	36.2
$C_5H_{10}O$	3,3-Dimethyloxetane	31.6
	Tetrahydropyran	32.2
$C_5H_{10}O_3$	1,3,6-Trioxacyclooctane	46.3
$C_8H_{16}O_4$	1,4,7,10-Tetraoxacyclododecane	63.2
$C_{10}H_{20}O_5$	1,4,7,10,13-Pentaoxacyclopentadecane	77.1
$C_3H_8O_2$	2-Methoxyethanol, methyl cellosolve®	42.7
$C_4H_{10}O_2$	2-Ethoxyethanol, cellosolve	45.8
$C_5H_{10}O_3$	Diethyl carbonate	41.1
	2-Methoxyethyl acetate methyl cellosolve acetate	47.8
$C_5H_{12}O_2$	Propoxyethanols	48—50
$C_6H_{12}O_3$	2-Ethoxyethyl acetate cellosolve acetate	50.2
	Ethoxymethyl propanoate	47.4
$C_6H_{14}O_2$	2-Butoxyethanol, butyl cellosolve	54.1
$C_7H_{14}O_3$	2-Propoxyethyl acetate	53.1
$C_8H_{16}O_3$	2-Butoxyethyl acetate, butyl cellosolve acetate	57.1
CS_2	Carbon disulfide	25.2
C_2H_6S	Dimethyl sulfide	26.5
$C_2H_6S_2$	Dimethyl disulfide	35.4
C_3H_8S	Ethyl methyl sulfide	29.5
$C_4H_{10}S$	Methyl propyl sulfide	33.8
	Isopropyl methyl sulfide	31.8
	Diethyl sulfide	33.4
$C_4H_{10}S_2$	Diethyl disufide	42.7
$C_5H_{12}S$	Dialkyl sulfides	33—38
$C_5H_{12}S_2$	Bis(ethylthio)methane	48.3
$C_6H_{14}S$	Dialkyl sulfides	37—43
$C_6H_{14}S_2$	1,2-Bis(ethylthio)ethane	57.0
	Dipropyl disulfide	56.7
$C_8H_{18}S$	Dialkyl sulfides	41—50
$C_8H_{18}S_2$	Dialkyl disulfides	52—60
C_2H_6S	Ethanethiol, ethyl mercaptan	25.1
$C_2H_6S_2$	1,2-Ethanedithiol	42.2
C_3H_8S	Propanethiols	27—30
C_3H_8S	1,3-Propanedithiol	47.2
$C_4H_{10}S$	1,4-Butanedithiol	29—34
$C_4H_{10}S_2$	Cyclopentanethiol	39.0
$C_5H_{12}S$	Pentanethiols	33—39
$C_5H_{12}S_2$	1,5-Pentanedithiol	56.8

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

Formula	Compound	$-U$/kJ mol^{-1}
C_6H_6S	Benzenethiol	45.1
$C_6H_{12}S$	Cyclohexanethiol	42.1
$C_{10}H_{22}S$	1-Decanethiol	63.0
C_3H_6S	Thiacyclobutane	33.5
C_4H_4S	Thiophene	32.3
C_4H_6S	Dihydrothiophenes	35—38
C_4H_8S	Thiacyclopentane	37.0
C_5H_6S	Methylthiophenes	36—37
$C_5H_{10}S$	Thiacyclohexane	40.1
CN_4O_8	Tetranitromethane	47.5
CH_3NO	Formamide	57.7
$CH_3 NO_2$	Nitromethane	35.9
C_2H_5NO	*N*-Methylformamide	53.7
C_3H_7NO	*N*-Ethylformamide	56.0
	N,N-Dimethylformamide	44.4
C_4H_9NO	*N*-Ethylacetamide	62.4
	N,N-Dimethylacetamide	47.8
	N-Methylpropionamide	62.4
	N,N-Diethylformamide	47.8
$C_5H_{11}NO$	*N*-Propylacetamide	67.3
	N-Isopropylacetamide	63.9
	N-Methylisobutyramide	64.6
$C_6H_5NO_2$	Nitrobenzene	52.5
$C_6H_9NO_3$	Triacetamide	57.9
$C_6H_{13}NO$	*N*-Butylacetamide	72.5
	N,N-Diethylacetamide	51.6
$C_6H_{14} N_2O$	*N*-Nitrosodipropylamine	49.2
$C_8H_8N_2O$	*N*-Nitroso-di-*tert*-buylamine	43.5
$C_{10}H_{11}NO_2$	*N,N*-Diacetylaniline	68.1
C_4H_8OS	Ethyl thiolethanoate	37.5
$C_5H_{10}OS$	Propyl thiolethanoate	41.6
	1-Methylethyl thiolethanoate	39.8
$C_6H_{10}OS$	Butyl thiolethanoate	45.6
	1,1-Dimethylethyl thiolethanoate	40.5
C_4H_5NS	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/cm³ mol⁻¹	$_l\Delta_g H$ or $_l\Delta_\infty H$ 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
$Si(CH_3)$	Tetramethylsilane, silicon tetramethyl	136	24.3	12.7
	Aliphatic Hydrocarbons			
C_5H_{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_6H_{14}	Hexane	132	31.7	14.9
C_7H_{16}	Heptane	148	36.6	15.1
C_8H_{18}	Octane	164	41.5	15.3
	Isooctane, 2,2,4-trimethylpentane	166	35.1	14.1
$C_{16}H_{34}$	Hexadecane	294	81.1	16.4
C_5H_{10}	Cyclopentane	95	28.7	16.6
C_6H_{12}	Cyclohexane	109	33.1	16.8
C_7H_{14}	Methylcyclohexane	128	35.4	16.0
C_6H_{12}	1-Hexene	126	30.7	14.9
C_8H_{16}	1-Octene	158	40.6	15.5
C_6H_{10}	1,5-Hexadiene	118	31.8	15.8
	Aromatic Hydrocarbons			
C_6H_6	Benzene	89	33.9	18.8
C_7H_8	Toluene, methylbenzene	107	38.0	18.2
C_8H_{10}	Ethylbenzene	123	42.3	18.0
	o-Xylene, 1,2-dimethylbenzene	121	43.4	18.4
	m-Xylene, 1,3-dimethylbenzene	123	42.7	18.0
	p-Xylene, 1,4-dimethylbenzene	124	42.4	18.0
C_9H_{12}	Propylbenzene	140	46.2	17.6
	Mesitylene, 1,3,5-trimethylbenzene	140	47.5	18.0
C_8H_8	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

δ/MPa$^{1/2}$

23.5
28.8
25.4
26.8

17.6
15.5
18.0
16.6
17.8
23.9

25.8
17.0
16.4
18.2
12.7

14.5
13.9
12.7
14.9
15.1
15.3
14.1
16.4
16.6
16.8
16.0
14.9
15.5
15.8

18.8
18.2
18.0
18.4
18.0
18.0
17.6
18.0
19.0
20.3
20.3
20.0

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

Formula	Substance	V/cm^3 mol^{-1}	$\Delta_g H$ or $\Delta_m H$ kJ mol^{-1}	δ/MPa$^{1/2}$
	Fluorocarbons			
C_6F_{14}	Perfluorohexane	205	32.4	12.1
C_7F_{16}	Perfluoroheptane	226	36.4	12.3
C_6F_{12}	Perfluorocyclohexane	170	28.9	12.5
C_7F_{14}	Perfluoro(methylcyclohexane)	196	33.1	12.5
	Other Fluorochemicals			
$(C_4F_9)_3N$	Perfluorotributylamine	360	54.4	12.7
$C_4Cl_2F_6$	Dichlorohexafluorocyclobutane	142	—	14.5
$C_4Cl_3F_7$	2,2,3-Trichloroheptafluorobutane	165	35.6	14.1
$C_2Cl_3F_3$	1,1,2-Trichloro-1,2,2,-trifluoroethane	120	27.5	14.5
$C_7F_{15}H$	Pentadecafluoroheptane	215	37.7	12.9
	Other Aliphatic Halogen Compounds			
CH_2Cl_2	Dichloromethane, methylene dichloride	64	28.6	20.0
$CHCl_3$	Trichloromethane, chloroform	81	31.0	18.8
CCl_4	Tetrachloromethane, carbon tetrachlorie	97	32.8	17.6
$CHBr_3$	Tribromomethane, bromoform	88	43.1	21.5
CH_3I	Iodomethane, methyl iodide	63	28.0	20.3
CH_2I_2	Diiodomethane, methylene diiodide	81	—	24.1
C_2H_5Cl	Chloroethane, ethyl chloride	74	23.8	17.0
C_2H_5Br	Bromoethane, ethyl bromide	75	27.2	18.2
C_2H_5I	Iodethane, ethyl iodide	81	32.2	19.2
$C_2H_4Cl_2$	1,2-Dichloroethane, ethylene dichloride	79	34.7	20.3
	1,1-Dichloroethane, ethylidene dichloride	85	32.2	18.6
$C_2H_4Br_2$	1,2-Dibromoethane, ethylene dibromide	90	41.4	20.9
$C_2H_3Cl_3$	1,1,1-Trichloroethane	100	32.6	17.4
$C_2H_2Cl_2$	*cis*-1,2-Dichloroethylene	76	28.9	18.6
	trans-1,2-Dichloroethylene	78	28.5	18.4
C_2Cl_4	Tetrachloroethylene	103	39.7	19.0
	Other Aliphatic Compounds			
CS_2	Carbon disulfide	61	28.0	20.5
$C_3H_8O_2$	Dimethoxymethane, methylal	89	27.6	16.8
$C_4H_{10}O$	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

	$V/cm^3\ mol^{-1}$	$\delta/MPa^{1/2}$
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

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

Thus, Equation 7 can be written

$$\pi = t\beta - p \qquad (8b)$$

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

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

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

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

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

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

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	a	a	—
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

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 Das[18-21] 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,

$$pV = RT \tag{12}$$

but the next best known is the van der Waals equation of state[24-26]

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

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

$$p + (\partial U/\partial V)_T = T(\partial p/\partial T)_V \tag{14}$$

$$p + a/V^2 \qquad = TR/(V - b) \tag{15}$$

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

$$(\partial U/\partial V)_T = a/V^2 \tag{16}$$

Integrating,

$$U = -a/V^2 \tag{17}$$

If $U = -{}_l\Delta_g{}^gU$ (Equation 3), then

$$a = V_l\Delta_g U = V^2 c = V^2 \delta^2 \tag{18}$$

and

$$(\partial U/\partial V)_T = {}_l\Delta_g U/V = c = \delta^2 \tag{19}$$

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]

$$U = -a/V^n \tag{20}$$

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

$$(\partial U/\partial V)_T = n({}_l\Delta_g U/V) \tag{21}$$

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

McGowan[33] 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

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

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

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

and the parameter $A = \delta^2 V^{1/3}\ \gamma^{-1}$ in Chapter 17 has been converted to $\text{mol}^{-1/3}$ from cal $\text{erg}^{-1}\ \text{mol}^{-1/3}$ 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	—

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

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:

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

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*, ${}^ia$, of component *i* follows from

$$RT \ln {}^ia = {}^i\mu - {}^i\mu^\circ \qquad (23)$$

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

$$\Delta_m S = -R \Sigma_i {}^i x \ln {}^i x \quad (24)$$

where ${}_i x$ is the mole fraction of component i. (Each mole fraction ${}^i x$ is less than unity, so $\ln {}^i x$ 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:

$$\Delta_m G = \Delta_m H - T\Delta_m S = RT \Sigma_i {}^i x \ln {}^i x \quad (25)$$

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 is[35]

$$^E\Delta_m G = \Delta_m G - RT \Sigma_i {}^i x \ln {}^i x \quad (26)$$

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

$$^E\Delta_m S = \Delta_m S + R\,({}^i x \ln {}^j x\, {}^i x \ln {}^j x) \quad (27)$$

An ideal mixture follows *Raoult's law*, which states that the partial pressure, ${}^i p$, of any component *i* is given by

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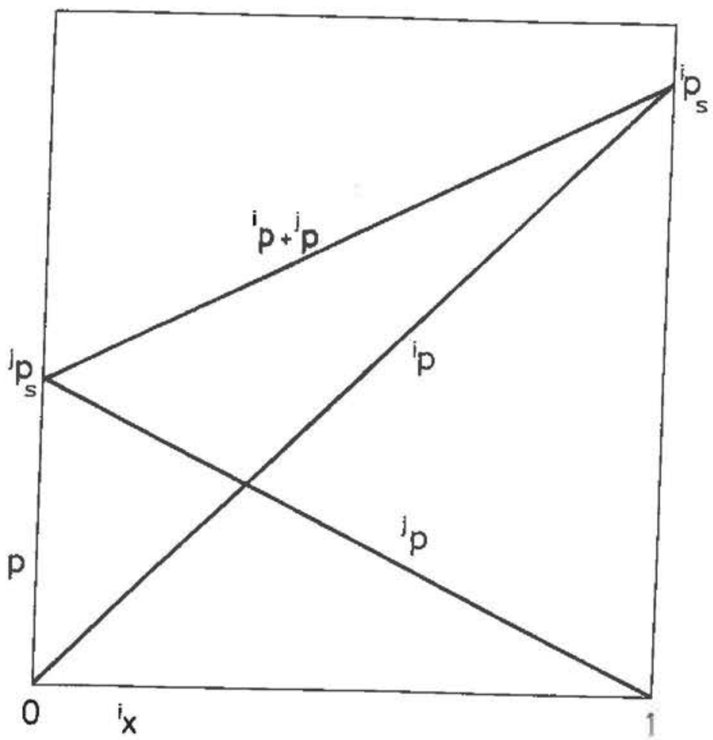

FIGURE 1. Total and partial vapor pressures in an ideal binary mixture at constant temperature.

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

where ${}^{i}x$ is the mole fraction of component i in the mixture and ${}^{i}p_s$ 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 ${}^{i}a$ of component i is not equal to its mole fraction value ${}^{i}x$, and it is therefore convenient to define the activity coefficient ${}^{i}f_x$ such that

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

The Gibbs free energy change on mixing is then expressed

$$\Delta_m G = RT\,\Sigma_i {}^{i}x \ln {}^{i}x + RT\,\Sigma_i {}^{i}a = \ln {}^{i}x + RT\,\Sigma_i {}^{i}x \ln {}^{i}f_x \tag{30}$$

and from Equation 26,

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

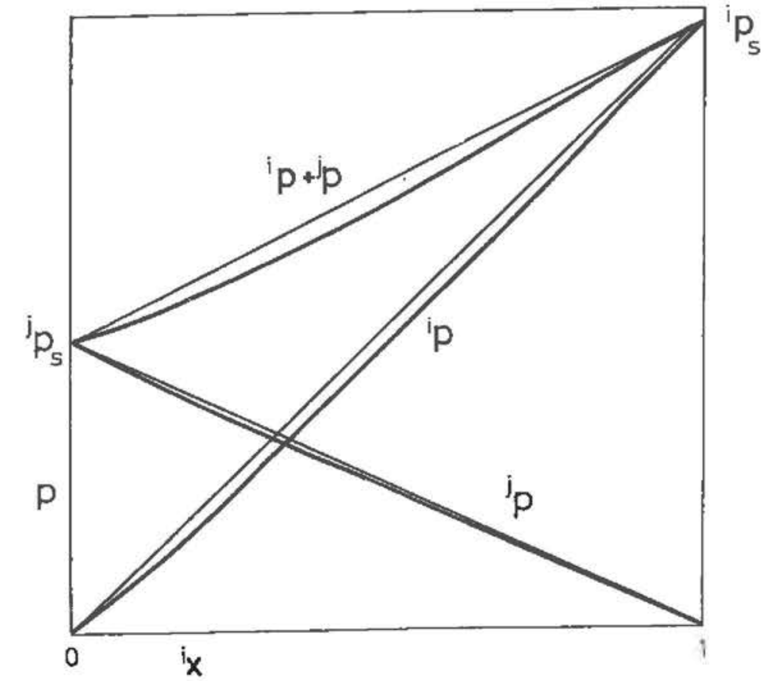

FIGURE 2. Total and partial vapor pressures at constant temperature for a system with negative deviations from Raoult's law.

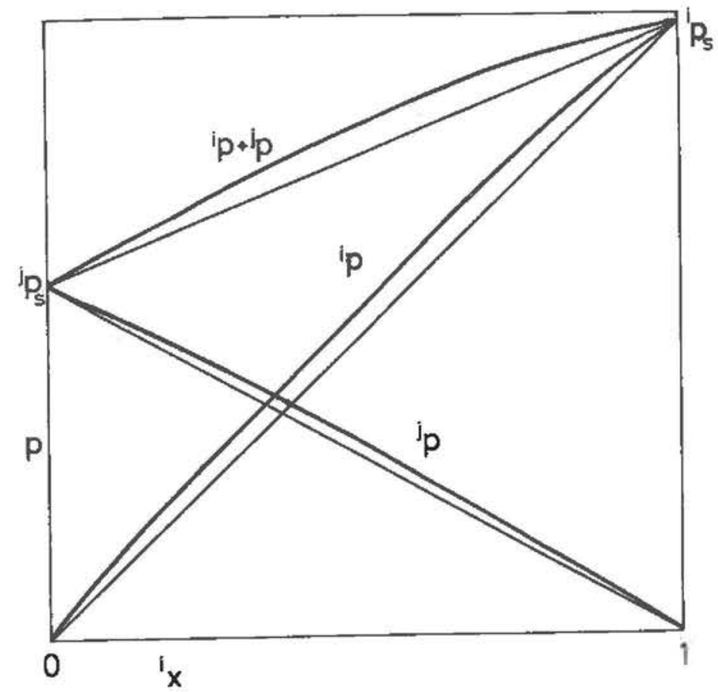

FIGURE 3. Total and partial vapor pressures at constant temperature for a system with moderate positive deviations from Raoult's law.

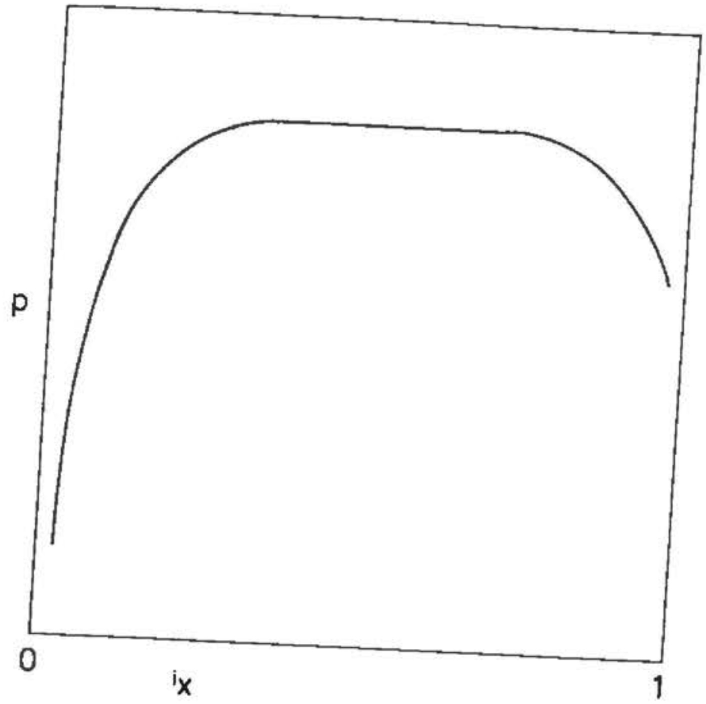

FIGURE 4. Total vapor pressure in equilibrium with a partially miscible pair of liquids, at constant temperature.

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

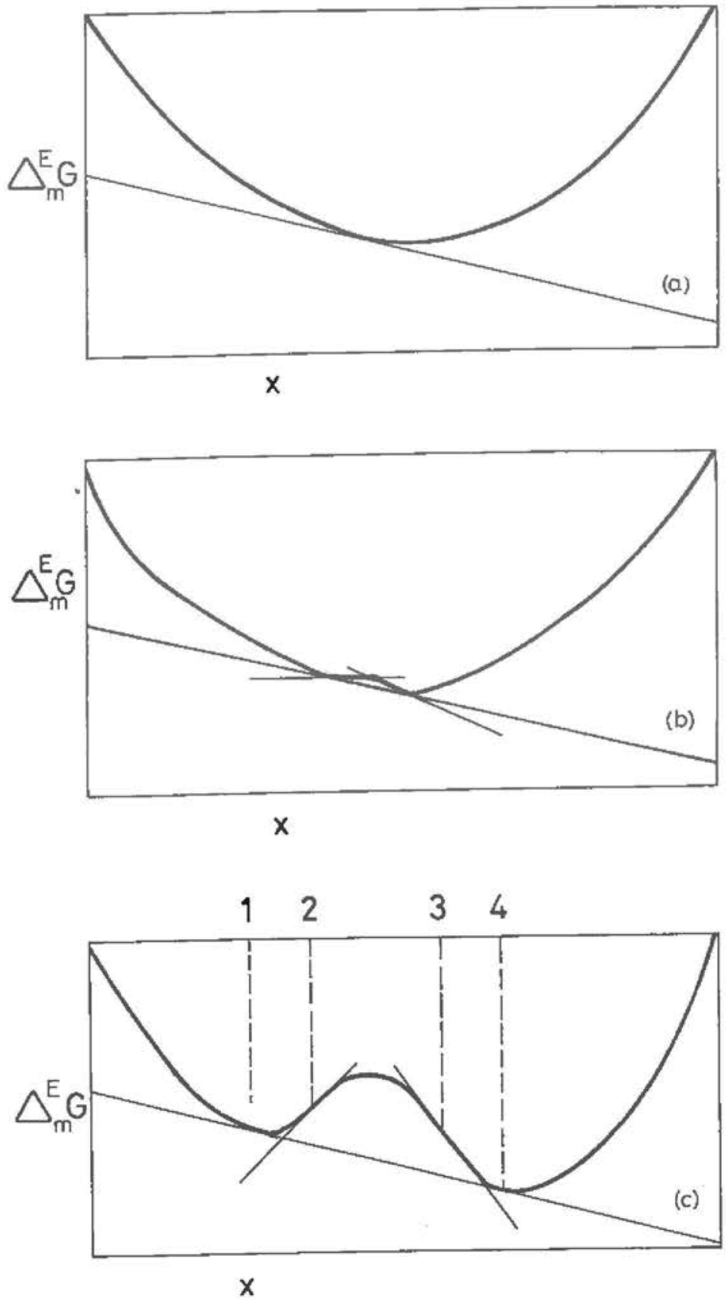

FIGURE 5. Excess Gibbs free energy of a binary mixture as a function of mole fraction: (a) miscibility in all proportions; (b) onset of demixing; (c) existence of two regions of stability, two regions of metastability, and one region of instability. (Adapted from Dayantis, J., *Plast. Mod. Elastomeres*,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

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Chapter 4

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

$$^{i}I + {}^{j}I \approx 2({}^{i}I\,{}^{j}I)^{1/2} \tag{1}$$

and

$$r \approx 2({}^{i}r\,{}^{j}r)^{1/2} \tag{2}$$

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

$$^{ij}U_{d} = {}^{i}U_{d}^{\,1/2}\,{}^{j}U_{d}^{\,1/2} \tag{3}$$

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 Carter[1] verified to within 1% the relationship

$$^{ij}a = ({}^{i}x\,{}^{i}a^{1/2} + {}^{j}x\,{}^{j}a^{1/2})^{2} \tag{4}$$

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

$$^{ij}a = {}^{i}x^{2}\,{}^{i}a + {}^{j}x^{2}\,{}^{j}a + 2\,{}^{i}x\,{}^{j}x\,{}^{ij}a \tag{4a}$$

if $^{ij}a = ({}^{i}a\,{}^{j}a)^{1/2}$. 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 continues[4-9]. 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 Waals[10] and van Laar,[11,12] was derived on semitheoretical grounds by Scatchard[13,14] and Hildebrand[15-19] 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

$$\Delta_m U_v = ({}^ix\,{}^iV + {}^jx\,{}^jV)\,{}^{ij}A\,{}^i\phi\,{}^j\phi \quad (5)$$

$$= {}^iV\,({}^ix + m\,{}^jx)\,{}^{ij}A\,{}^i\phi\,{}^j\phi \quad (6)$$

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:

$$m = {}^jV/{}^iV = ({}^jM/{}^iM)({}^i\rho/{}^j\rho) \quad (7)$$

$${}^i\phi = {}^iV\,{}^ix/({}^jV\,{}^jx + {}^iV\,{}^ix) = {}^ix/(m\,{}^jx + {}^ix) \quad (8)$$

$${}^j\phi = {}^jV\,{}^jx/({}^jV\,{}^jx + {}^iV\,{}^ix) = m\,{}^jx/(m\,{}^jx + {}^ix) \quad (9)$$

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. ${}^{ij}A$ 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

$${}^{ij}A = {}^ic + {}^jc - 2\,{}^{ij}c \quad (10)$$

where the ${}^{ij}c$ 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 ${}^{ij}A$ is not simply the difference between the cohesive pressure of components i and j; this quantity (${}^ic - {}^jc$) has been termed [36] the "mutual cohesion factor", but has not proved of great value in correlating the properties of materials.

The interchange cohesive pressure ${}^{ij}A$ 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 ${}^{ij}A$ 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

$${}^i\delta^2 = {}^ic = \Delta\,{}^iU/{}^iV \text{ and } {}^j\delta^2 = {}^jc = \Delta\,{}^jU/{}^jV \quad (11)$$

Using the geometric mean approximation, Equation 3,

$${}^{ij}c = ({}^ic\,{}^jc)^{1/2} \quad (12)$$

so

$${}^{ij}A = ({}^ic^{1/2} - {}^jc^{1/2})^2 = ({}^i\delta - {}^j\delta)^2$$

$$= {}^i\delta^2 + {}^j\delta^2 - 2\,{}^{ij}c \quad (13)$$

and the Hildebrand-Scatchard equation can be written

$$\Delta_m U_v = ({}^ix\,{}^iV + {}^jx\,{}^jV)\,{}^{ij}A\,{}^i\phi\,{}^j\phi$$
$$= ({}^ix\,{}^iV + {}^jx\,{}^jV)\,({}^i\delta - {}^j\delta)^2\,{}^i\phi\,{}^j\phi \qquad (14)$$

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 coefficient ^{j} is

$$RT \ln {}^jf_x = RT \ln ({}^ja/{}^jx) = {}^jV\,{}^i\phi^2\,{}^{ij}A = {}^jV\,{}^i\phi^2\,({}^i\delta - {}^j\delta)^2 \qquad (15)$$

Similarly,

$$RT \ln {}^if_x = RT \ln ({}^ia/{}^ix) = {}^iV\,{}^j\phi^2\,{}^{ij}A = {}^jV\,{}^j\phi^2\,({}^i\delta - {}^j\delta)^2 \qquad (15a)$$

Expanding Equation 15,

$$RT \ln {}^jf_x = {}^jV/[({}^iV\,{}^ix)\,/\,({}^jV\,{}^j \propto + {}^iV\,{}^ix)]^2\,({}^i\delta - {}^j\delta)^2 \qquad (15b)$$

In dilute solutions, ${}^jV{}^jX \ll {}^iV{}^iX$, and in infinitely dilute solutions ${}^i\phi = 1$, so

$$RT \ln {}^jf_x^\infty = {}^jV\,{}^{ij}A = {}^jV\,({}^i\delta - {}^j\delta)^2 \qquad (16)$$

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

$$RT \ln {}^jf_x^\infty = {}^jV\,({}^i\delta - \bar{\delta})^2 \qquad (17)$$

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 $-R \ln {}^ix$ in the entropy of mixing with

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

and leads to

$$RT \ln {}^if_x = {}^iV\,{}^j\phi^2\,{}^{ij}A + RT[\ln {}^i\phi/x + {}^j\phi(1 - {}^iV/{}^jV)] \qquad (18)$$

or

$$\ln {}^ia = {}^iV\,{}^j\phi^2\,{}^{ij}A/(RT) + \ln {}^i\phi + {}^j\phi\,(1 - {}^iV/{}^jV) \qquad (19)$$

For solute j,

$$RT \ln {}^jf_x = {}^jV\,{}^i\phi^2\,{}^{ij}A + RT[\ln {}^j\phi/{}^jx + {}^i\phi(1 - {}^jV/{}^iV)] \qquad (20)$$

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

$$RT \ln {}^j f_x^\infty = {}^jV\, {}^{ij}A + RT[\ln({}^jV/{}^iV) + 1 - {}^jV/{}^iV] \tag{21}$$

or

$$\ln {}^j f_x^\infty = {}^jV/(RT)\, {}^{ij}A + {}^{ij}d \tag{21a}$$

where the Flory-Huggins combinatorial size effect term is

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

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),

$$\Delta_m G = {}^E\Delta_m G + {}^I\Delta_m G = RT\,({}^ix \ln {}^ix\, {}^if_x + {}^jx \ln {}^jx\, {}^jf_x) \tag{22}$$

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

$$\Delta_m G/(RT) = ({}^ix\, {}^iV + {}^jx\, {}^jV)\, {}^{ij}A\, {}^i\phi\, {}^j\phi + {}^ix \ln {}^ix + {}^jx \ln {}^jx \tag{23}$$

$$\Delta_m G/(RT) = [{}^ix\, {}^jx\, {}^iV\, {}^jV\, ({}^i\delta - {}^i\delta)^2]/({}^ix\, {}^iV + {}^jx\, {}^jV) + {}^ix \ln {}^ix + {}^jx \ln {}^jx \tag{23a}$$

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

$${}^ix = [{}^iV - ({}^iV^2 + {}^jV^2 - {}^iV\, {}^jV)^{1/2}]/({}^iV - {}^jV) \tag{24}$$

$$T_{cs} = 2\, {}^ix\, {}^jx\, {}^iV^2\, {}^jV^2\, {}^{ij}A/[R({}^ix\, {}^iV + {}^jx\, {}^jV)^3] \tag{25}$$

or

$$T_{cs} = 2\, {}^ix\, {}^jx\, {}^iV^2\, {}^jV^2\, ({}^i\delta - {}^i\delta)^2/[R({}^ix\, {}^iV + {}^jx\, {}^jV)^3] \tag{25a}$$

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

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

The relationships between T_{cs} and δ for hydrocarbons and film-forming materials have been explored by Mandik[38]. The rest of the liquid (1)-liquid (2) phase boundary can also be determined, with the equations

$$RT \ln({}^ix_1/{}^ix_2) = {}^jV\, ({}^j\phi_2{}^2 - {}^j\phi_1^2)({}^i\delta - {}^j\delta)^2 \tag{27}$$

$$RT \ln({}^jx_1/{}^jx_2) = {}^iV\, ({}^i\phi_2{}^2 - {}^i\phi_1^2)({}^i\delta - {}^j\delta)^2 \tag{27a}$$

or by means of the corresponding equations with ${}^{ij}A$ replacing $({}^i\delta - {}^i\delta)^2$. The experimental UCST may be used to evaluate ${}^{ij}A$, 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

$$T_{cs} = 2\ {}^{ij}A\ {}^{i}V\ {}^{j}V/({}^{i}V^{1/2} + {}^{j}V^{1/2})^2$$

or

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

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 ${}^{j}f_x = {}^{j}f^{\infty}$, Equation 21 can be written in terms of the mole fraction solubility of j in i, ${}^{j}x_s$ (solubility of water in the organic phase):

$$-RT \ln {}^{j}x_s = {}^{j}V\ {}^{ij}A + RT(\ln {}^{j}V \mid {}^{i}V + 1 - {}^{j}V \mid {}^{i}V) \qquad (29)$$

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

$$-RT \ln {}^{j}x_s = {}^{j}V\ {}^{ij}A \qquad (29a)$$

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

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

and the value of ${}^{ij}c$ 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

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

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

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 incoporate 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. Lee[45] 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 Scigliano[42] have demonstrated this in the case of a mixture of two typical organic liquids, both with $V = 100\ \mathrm{cm^3\ mol^{-1}}$, but with ΔU values of 3.3 and 3.8 $\mathrm{mol^{-1}}$. 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 extension[50-52] 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

$$|{}^{j}\delta - {}^{i}\delta|/\mathrm{MPa}^{1/2} \le 5 \le |{}^{k}\delta - {}^{j}\delta|/\mathrm{MPa}^{1/2}$$

as observed for diamyl ether-acetonitrile-glycerol.[53] In a few cases, vaporization enthalpies (1,4-dioxane-water,[54] hexane-cyclohexanone[55]) or condensation enthalpies (trichloromethane-acetone, trichloromethane-ether[56]) 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

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

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 ${}^{i}\delta$ and ${}^{j}\delta$ of the two component liquids, the solute should be completely miscible when the ratio ${}^{i}\phi/{}^{j}\phi$ 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,

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

so if ${}^{k}\phi$ is small,

and

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

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

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

The more general expression for the effective Hildebrand parameter is

$$\bar{\delta} = \Sigma_i\,{}^{i}\phi\,{}^{i}\delta/\Sigma_i\,{}^{i}\phi \qquad (32b)$$

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]

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

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 (δ = 15.1 MPa$^{1/2}$) and ethanol (δ = 26.0 MPa$^{1/2}$) as a solvent mixture for cellulose nitrate (δ = 23 MPa$^{1/2}$). However, frequently when the solute solubility (${}^{k}x_s$) 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 ${}^{k}x_s$ 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 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]

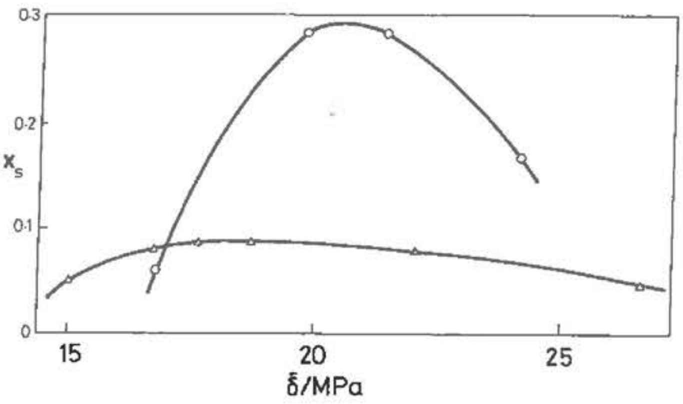

FIGURE 1. Variation in the solubility of 2-nitro-5-methylphenol as a function of the effective Hildebrand parameter of the binary solvent mixtures cyclohexane-diiodomethane (○) and ethanol-hexane (△) at 25°C. (Adapted from Buchowski, H., Domanska, U., and Ksiazczak, A., *Pol. J. Chem.*, 53, 1127, 1979.)

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 Walkley[68] attempted to improve on Equation 32 by defining an effective volume fraction, ϕ^*, which reflects the preferential "solvation" by one of the liquid components:

$$\bar{\delta} = {}^i\delta\, {}^i\phi^* + {}^j\delta\, {}^j\phi^* \tag{33}$$

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

$${}^i\phi^* + {}^j\phi^* = 1 \tag{33a}$$

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

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

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's[69] idea of a Boltzmann factor in the enthalpy of complex formation was proposed by Nakanishi and Asakura[70] 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 mixture[29] the excess Gibbs free energy of mixing is

$${}^E\Delta_m G = (\Sigma_i\, {}^ix\, {}^iV)({}^1/_2\, \Sigma_i\, \Sigma_j\, {}^{ij}A\, {}^i\phi) + RT\, \Sigma_i\, {}^ix \ln ({}^i\phi/{}^ix) \tag{35}$$

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

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

then

$$ {}^E\Delta_m G = (\Sigma_i\, {}^ix\, {}^iV)({}^1/_2\, \Sigma_i\, \Sigma_j\, {}^{ij}A\, {}^i\phi\, {}^j\phi) \tag{36} $$

The activity coefficient of component n is obtained from the partial derivative (constant T, p, and ${}^in$ for $i \neq k$)

$$ RT \ln({}^ka/{}^kx) = RT \ln {}^kf_x = [(\partial\, {}^tn\, {}^E\Delta_m G)/\partial\, {}^kn] \tag{37} $$

where ${}^in$ is the amount of substance i and ${}^tn$ is the total amount of substance. This can be shown to be

$$ RT \ln {}^kf_x = {}^kV\, \Sigma_i\Sigma_j\, ({}^{ik}A - {}^1/_2\, {}^{ij}A)\, {}^i\phi\, {}^j\phi + RT\, [\ln ({}^k\phi/{}^kx) + 1 - {}^k\phi/{}^kx] \tag{38} $$

Only if ${}^ix = {}^i\phi$ for all i does this equation reduce to

$$ RT \ln {}^kf_x = {}^kV\, \Sigma_i\, \Sigma_j\, ({}^{ik}A - {}^1/_2\, {}^{ij}A)\, {}^i\phi\, {}^j\phi \tag{39} $$

and with Equation 13,

$$ RT \ln {}^kf_x = {}^kV\, ({}^k\delta - \bar{\delta})^2 \tag{40} $$

where the effective Hildebrand parameter of the mixture is

$$ \bar{\delta} = \Sigma_i\, {}^i\phi\, {}^i\delta \tag{41} $$

the summation extending over all components, including the solute k when the volume fraction ${}^k\phi$ 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 Rigbi[72] and by Froehling and Hillegers.[73] Behnken[74] 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

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

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 used[75] 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
o-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 of the swelling of a slightly cross-linked analog of the polymer of

TABLE 2
Hildebrand Parameters and Molar Volumes for Cholesterol and Triglycerides

		$\delta/MPa^{1/2}$	$V/cm^3\ mol^{-1}$
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., Makhlouf, 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 $({}^{ij}g - {}^{ii}g)$ and $({}^{ij}g - {}^{jj}g)$.

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).

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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 Hansen[9-30] 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 ${}^{ij}c$ 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

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

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

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

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

$${}^{ij}c_d = ({}^{i}c_d\,{}^{j}c_d)^{1/2} = {}^{i}\delta_d\,{}^{j}\delta_d \qquad (2)$$

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

$$^{ij}A_d = {}^i\delta_d^2 + {}^j\delta_d^2 - 2\,{}^i\delta_d\,{}^j\delta_d = ({}^i\delta_d - {}^j\delta_d)^2 \tag{3}$$

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

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

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 Jensen[35] 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 ${}^ic_o$, and the corresponding orientation cohesion parameter, ${}^i\delta_o$, is defined by

$$-\,{}^iU_o \,/\, {}^iV = {}^ic_o = {}^i\delta_o^2 \tag{5}$$

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

$$^{ij}c_o = ({}^ic_o\,{}^jc_o)^{1/2} = {}^i\delta_o\,{}^j\delta_o \tag{6}$$

The interchange cohesive pressure due to orientation is

$$^{ij}A_o = ({}^i\delta_o - {}^j\delta_o)^2 \tag{7}$$

Keller, Karger, and Snyder[5] and Munafo, Buchmann, Hô Nam-Tran and Kesselring[37] 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 ${}^i\delta_i\,{}^i\delta_d$, where ${}^i\delta_i$ is the induction cohesion parameter. Similarly, in a mixture of i and j

$$ {}^{ij}c_i = {}^i\delta_i\,{}^j\delta_d + {}^j\delta_i\,{}^i\delta_d \tag{8} $$

Therefore it can be shown that

$$ {}^{ij}A_i = 2\,{}^i\delta_i\,{}^i\delta_d + 2\,{}^j\delta_i\,{}^j\delta_d - 2\,{}^j\delta_i\,{}^i\delta_d - 2\,{}^i\delta_i\,{}^j\delta_d \tag{9} $$

$$ = 2({}^i\delta_d - {}^j\delta_d)({}^i\delta_i - {}^j\delta_i) \tag{10} $$

5.4 LEWIS ACID-BASE

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

A	+	D	⇌	$\overset{\delta-}{A}\ldots\ldots\overset{\delta+}{D}$
Lewis acid		Lewis base		Lewis acid-base complex
Electron-pair acceptor (EPA)		Electron-pair donor (EPD)		Addition compound
Electrophile		Nucleophile		Adduct

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:

$$ {}^{ij}A_{ab} = 2\,({}^{i}\delta_a - {}^{j}\delta_a)({}^{i}\delta_b - {}^{j}\delta_b) \tag{12} $$

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

$$ {}^{i}\delta_a = {}^{j}\delta_b = 0,\ {}^{ij}A_{ab} = -2\,{}^{j}\delta_a\,{}^{i}\delta_b \tag{13} $$

and when

$$ {}^{j}\delta_a = {}^{i}\delta_b = 0,\ {}^{ij}A_{ab} = -2\,{}^{i}\delta_a\,{}^{j}\delta_b \tag{14} $$

When ${}^{ij}A_{ab}$ 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 parameters[56] 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:

R—X—H	+	:Y—R	⇋	R—X—H......Y=R	
Electron-pair acceptor (EPA)		Electron-pair donor (EPD)		Hydrogen bond	
Proton donor		Proton acceptor			(15)
Hydrogen-bond donor		Hydrogen-bond acceptor			
Brönsted acid		Base			

The classification by Pimentel and McClellan[58] 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, ${}^{ij}A_{ab}$. Any net increase in the extent of hydrogen bonding as a result of mixing decreases ${}^{ij}A_{ab}$ 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.

$$ {}^{ij}A_{ab} = 2\,({}^{i}\delta_a - {}^{j}\delta_a)({}^{i}\delta_b - {}^{j}\delta_b) \tag{17} $$

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.

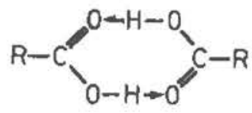
Variations in properties resulting from hydrogen-bonding interactions can be looked at from other points of view. Chastrette and co-workers[63] have observed from multivariate statistical analysis of solubility information that a liquid may have more than one point in hyperspace associated with it: for 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 Chen[66] 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,

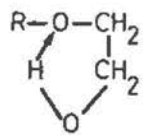
$$ {}^{E}\Delta_m G = {}^{E}\Delta_m G_C + {}^{E}\Delta_m G_P \tag{18} $$

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 Cavé[68] 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 manner[69] illustrated in Equation 20, Chapter 6. Examples are carboxylic acids,

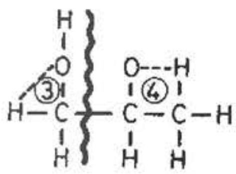


and glycol ethers such as Cellosolves® and Carbitols®



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. Hoy[69] 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. Nisbet[75] 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 Cohen[73] 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 ${}^{ij}K$ (see Section 5.7):

$$ {}^j\Lambda^2 = {}^j\delta^2 + {}^j\Gamma^2 \qquad (19) $$

The variable cohesion parameter of a solute obtained from observations of interactions with relatively polar liquids would then be designated not ${}^j\delta$ but ${}^j\Lambda$, 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 Abraham[74] 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:

$$^{ij}A = {}^{ij}A_d + {}^{ij}A_o + {}^{ij}A_i + {}^{ij}A_{ab} \tag{20}$$

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

$$= {}^i\delta_t^2 + {}^j\delta_t^2 - 2\,{}^i\delta_d{}^j\delta_d - 2\,{}^i\delta_o{}^j\delta_o - 2{}^i\delta_i\,{}^j\delta_d - 2\,{}^j\delta_i\,{}^i\delta_d - 2\,{}^i\delta_a{}^j\delta_b - 2\,{}^j\delta_a{}^i\delta_b \tag{22}$$

where ${}^i\delta_t$ 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

$${}^i\delta_t^2 = {}^i\delta_d^2 + {}^i\delta_o^2 + 2\,{}^i\delta_i{}^i\delta_d + 2\,{}^i\delta_a{}^i\delta_b \tag{23}$$

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

$$\delta^2 = \delta_d^2 + \delta_o^2 + 2\delta_i\delta_d + 2\delta_a\delta_b \tag{24}$$

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:

$$^{ij}c = ({}^ic\,{}^jc)^{1/2} = {}^i\delta\,{}^j\delta \tag{25}$$

The approach taken by Karger, Snyder, and Eon[4] 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 δ_a δ_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, they[161]

TABLE 1
Five-Component Cohesion Parameters of Liquids in Order of Increasing Hildebrand Parameter[1-4]

	δ/MPa$^{1/2}$						V/cm^{3}mol^{-1}
Liquid	δ_t	δ_d	δ_o	δ_i	δ_a	δ_b	
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
N,N-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
N,N-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	$\delta/\mathrm{MPa}^{1/2}$					
	δ_d	δ_o	δ_i	δ_a	δ_b	δ_t
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, *sec*-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	$\delta/\mathrm{MPa}^{1/2}$						
	δ_d^{a}	δ_o^{b}	δ_i^{b}	δ_p^{c}	δ_h^{d}	δ_t^{e}	δ_t^{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] $\delta_p^2 = \delta_o^2 + 2\delta_i\,\delta_d$
[d] $\delta_h^2 = \delta_t^2 - \delta_d^2 - \delta_p^2$
[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 Kesselring[37] (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. Walker[83] proposed the dimensionless specific interchange coefficient, ${}^{ij}K$, which has values between 0.98 and 1.06 for many liquids,

$$ {}^{ij}c = {}^{ij}K\,({}^{i}c\,{}^{j}c)^{1/2} \tag{26} $$

so

$$ {}^{ij}A = {}^{i}c + {}^{j}c - 2\,{}^{ij}K\,{}^{i}c^{1/2}\,{}^{j}c^{1/2} \tag{27} $$

$$ = {}^{i}\delta^2 + {}^{j}\delta^2 - 2\,{}^{ij}K\,{}^{i}\delta\,{}^{j}\delta \tag{28} $$

This parameter was given the symbol f by Reed[84,85] and Sonnich Thomsen[86-88] and also divided into several factors corresponding to different correction terms. Prausnitz and coworkers and others[89-93] used the dimensionless constant ${}^{ij}l$ (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,

$$ {}^{ij}c = ({}^{i}c\,{}^{j}c)^{1/2}\,(1 - {}^{ij}l) \tag{29} $$

and of course this is related to ${}^{ij}K$ by

$$ {}^{ij}l = 1 - {}^{ij}K \tag{30} $$

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

$$ {}^{ij}A = ({}^{i}\delta - {}^{j}\delta)^2 + 2\,{}^{ij}l\,{}^{i}\delta\,{}^{j}\delta \tag{31} $$

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

Martin et al.[94-96] in studies of drug solubilities proposed the binary interaction parameter ${}^{ij}W$, which in terms of ${}^{ij}A$ is defined by

$$ {}^{ij}A = ({}^{i}\delta^2 + {}^{j}\delta^2 - 2\,{}^{ij}W) = ({}^{i}\delta - {}^{j}\delta)^2 + 2\,({}^{i}\delta\,{}^{j}\delta - {}^{ij}W) \tag{32} $$

They also showed[97] that these parameters are simply three different representations of deviations from the geometric mean mixing approximation,

$$ 1 - {}^{ij}l = {}^{ij}W/({}^{i}\delta\,{}^{j}\delta) = {}^{ij}K \tag{33a} $$

or

TABLE 4
Binary Interaction Parameters for Solutes in Cryogenic Liquids

Solute(*j*)-solvent(*i*)	^{ij}l	Recommended range for use of given ^{ij}l, *T*/K	Maximum error, $100\lvert {}^{j}x_{obs} - {}^{j}x_{calc}\rvert / {}^{ij}X_{obs}$
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.

$$^{ij}W = {}^{ij}K\, {}^{i}\delta\, {}^{j}\delta \tag{33b}$$

Although values of ^{ij}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 $^{ij}\delta'$ defined such that

$$^{ij}\delta' = {}^{ij}W^{1/2} = ({}^{ij}K\, {}^{i}\delta\, {}^{j}\delta)^{1/2} = (1 - {}^{ij}l)^{1/2}\, ({}^{i}\delta\, {}^{j}\delta)^{1/2} \tag{34}$$

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

Mikos and Peppas[165] employed the geometric mean correction parameter ^{ij}l in the correlation of polymer-liquid interaction parameters (Section 13.5) for hydrophilic copolymers with water, using

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

with ^{ij}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 ^{ij}W by the parabolic relationship[73]

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

The geometric mean corrections ^{ij}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 ^{ij}l and infrared carbonyl stretching frequencies.[100]

It is apparent that $^{ij}\delta'$, ^{ij}l, ^{ij}K, and ^{ij}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

$$RT \ln {}^jf_x = {}^jV\,{}^i\phi^2\{({}^i\delta - {}^j\delta)^2 + 2\,{}^{ij}l\,{}^i\delta\,{}^j\delta\} \qquad (36)$$

They also may be determined from gas phase data[88,92,101-105] where

$$^{ij}T_c = ({}^iT_c\,{}^jT_c)^{1/2}\,(1 - {}^{ij}k) \qquad (37)$$

Although the parameters ^{ij}l and ^{ij}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, Pauling[106] suggested

$$^{ij}E/\text{ kJ mol}^{-1} = ({}^iE\,{}^jE)^{1/2}/\text{ kJ mol}^{-1} + 125({}^iX - {}^jX)^2 \qquad (38)$$

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

$$^{ij}c = ({}^ic\,{}^jc)^{1/2} + k({}^iX - {}^jX)^2/({}^iV\,{}^jV)^{1/2} \qquad (39)$$

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:

$$RT \ln {}^jf_x = {}^{ij}A\,{}^jV\,{}^i\phi^2 \qquad (40)$$

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

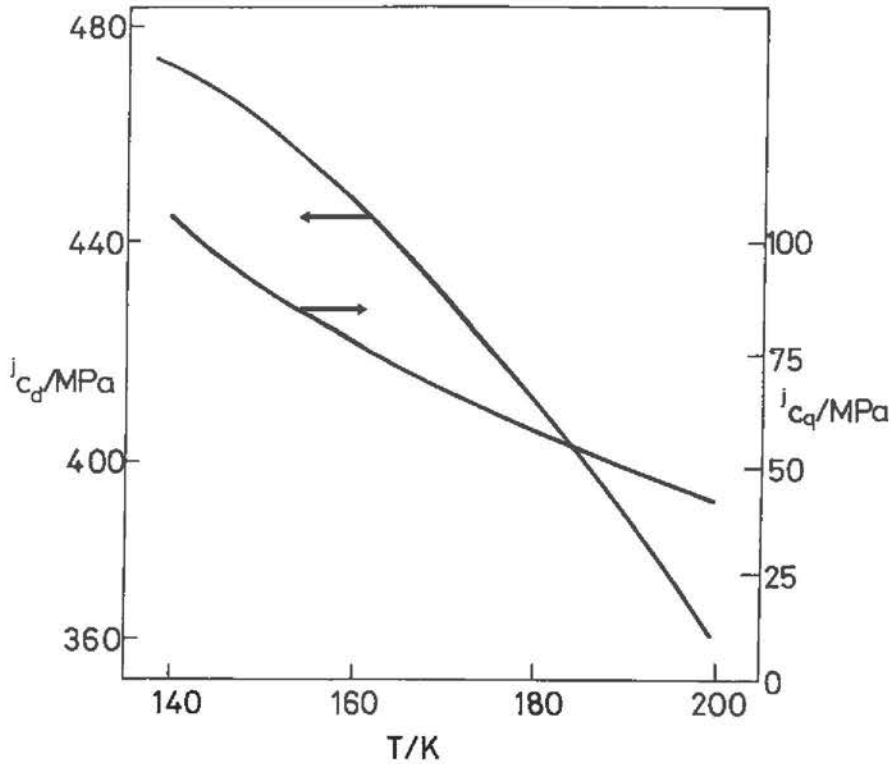


FIGURE 1. Dispersion and quadrupole cohesive pressures of subcooled liquid carbon dioxide as functions of temperature. (Adapted from Myers, A. L. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 4, 209, 1965.)

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:

$$ {}^jc = {}^jc_d + {}^jc_q \text{ and } {}^ic = {}^ic_d + {}^ic_q \qquad (41) $$

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, ${}^{ij}c_q$ was evaluated from theoretical expressions, and the total cohesive pressure was given by

$$ {}^{ij}c = ({}^ic_d\,{}^jc_d)^{1/2} + {}^{ij}c_q + {}^{ij}c_{ab} \qquad (42) $$

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, ${}^{ij}c_{ab}$ rises with falling temperature and becomes relatively more important in such low temperature systems. The full expression for the interchange cohesive pressure is thus

$$ \begin{aligned} {}^{ij}A &= {}^ic + {}^jc - 2\,{}^{ij}c \\ &= {}^ic + {}^jc - 2\,[({}^ic_d\,{}^jc_d)^{1/2} + {}^{ij}c_q] \end{aligned} \qquad (43) $$

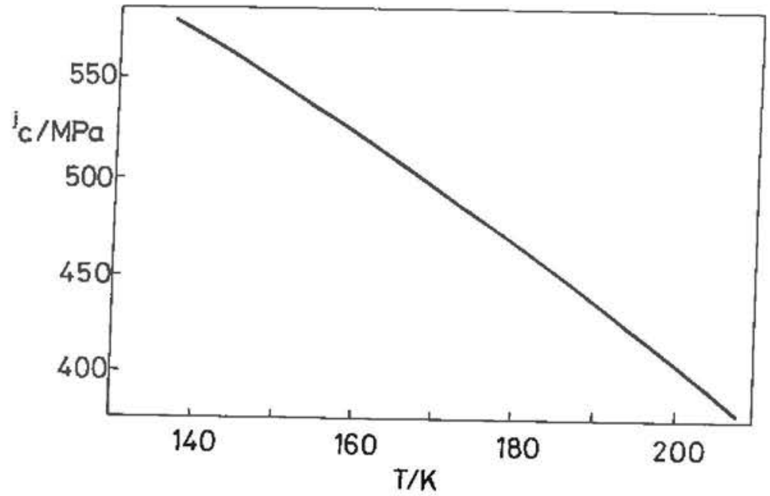


FIGURE 2. Cohesive pressure of subcooled liquid carbon dioxide as a function of temperature. (Adapted from Myers, A. L. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 4, 209, 1965.)

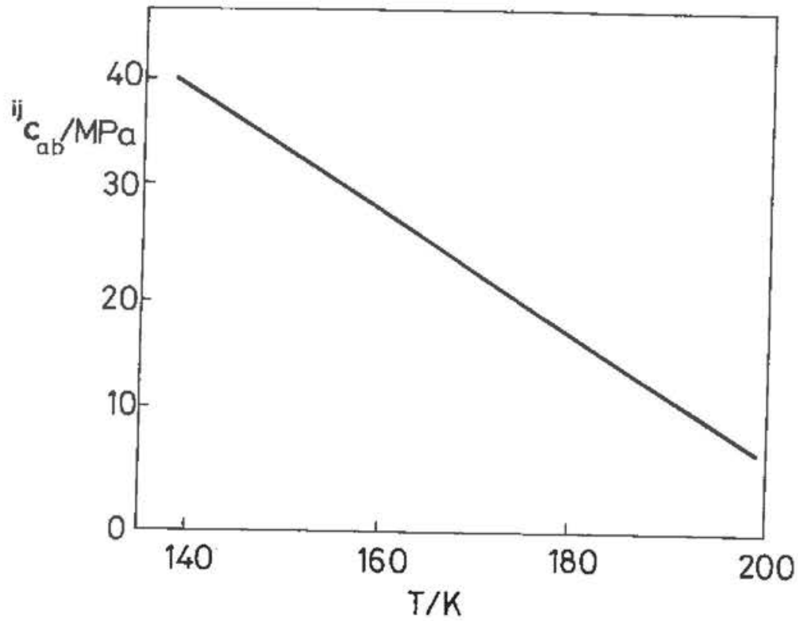


FIGURE 3. Acid-base complex contribution to the cohesive pressure of carbon dioxide-alkene mixtures as a function of temperature. (Adapted from Myers, A. L. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 4, 209, 1965.)

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_λ) and a polar parameter (δ_τ). 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

$$\delta^2 = \delta_\lambda^2 + \delta_\tau^2 \tag{44}$$

and comparison with Equation 24 suggests that δ_λ can be identified with δ_d and that δ_τ corresponds to δ_o.

In their evaluation of δ_λ and δ_τ for polar liquids, Blanks and Prausnitz[110] 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 Winkle[115] (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),

$$^{ij}A = {}^ic + {}^jc - 2\,{}^{ij}c = {}^i\delta_\lambda^2 + {}^j\delta_\lambda^2 - 2\,{}^i\delta_\lambda{}^j\delta_\lambda \tag{45}$$

$$= ({}^i\delta_\lambda - {}^j\delta_\lambda)^2 = ({}^i\delta - {}^j\delta)^2 \tag{46}$$

as used in Equation 13, Chapter 4.

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

$$^{ij}A = {}^ic + {}^jc - 2\,{}^{ij}c = {}^i\delta_\tau^2 + {}^i\delta_\lambda^2 + {}^j\delta_\lambda^2 - 2\,({}^i\delta_\lambda\,{}^j\delta_\lambda + {}^{ij}\Psi) \tag{47}$$

$$= ({}^i\delta_\lambda - {}^j\delta_\lambda)^2 + {}^i\delta_\tau^2 - 2\,{}^{ij}\Psi \tag{48}$$

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/cm³ mol⁻¹	δ/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
cis-2-Butylene	91.2	14.7
trans-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
o-Xylene, 1,2-dimethylbenzene	121.2	18.4
m-Xylene, 1,3-dimethylbenzene	123.5	18.0
p-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 tetrachloride	97.1	17.6

[a] Estimated from gas solubility data.[114]

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

$$^{ij}A = (^i\delta_\lambda - {}^j\delta_\lambda)^2 + (T_*/T)\,{}^i\delta_\tau^2 - 2\,{}^{ij}\Psi \qquad (49)$$

where T_* 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, $^{ij}\Psi$, 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 difference[110] 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 $^{ij}\Psi$ as proportional to the square of the polar cohesion parameter $^i\delta_\tau^{\,2}$:

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

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 Prausnitz[113] 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/cm^3mol^{-1}	Nonpolar, $\delta_\lambda/MPa^{1/2}$	Polar, $\delta_\tau/MPa^{1/2}$	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/°C	V/cm^{3}mol^{-1}	δ_λ/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
p-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/°C	V/cm^{3}mol^{-1}	Nonpolar, δ_λ/MPa$^{1/2}$	Polar, δ_τ/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	$t/^\circ C$	V/cm^3mol^{-1}	Nonpolar, $\delta_\lambda/MPa^{1/2}$	Polar, $\delta_\tau/MPa^{1/2}$
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
N,N-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
N,N-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
	100	72.9	15.2	17.7
Nitromethane	25	54.3	16.5	19.3
	45	55.3	16.2	18.9
	60	56.3	15.9	18.5
	100	59.3	15.2	17.6
Dimethylsulfoxide	25	71.3	17.5	19.4

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

$${}^{ij}A = ({}^{i}\delta_\lambda - {}^{j}\delta_\lambda)^2 + ({}^{i}\delta_\tau - {}^{j}\delta_\tau)^2 \qquad (50)$$

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

$${}^{ij}A = ({}^{i}\delta_\lambda - {}^{j}\delta_\lambda)^2 + (T_*/T)({}^{i}\delta_\tau - {}^{i}\delta_\tau)^2 \qquad (51)$$

Helpinstill and Van Winkle[115] extended the correlation of Weimer and Prausnitz[113] to polar-polar situations, defining the new parameter ${}^{ij}\psi$ 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/°C	V/cm^{3}mol^{-1}	Nonpolar, δ_λ/MPa$^{1/2}$	Polar, δ_τ/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
	100	131.4	13.5	0.0
1-Pentene	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
	100	121.6	13.5	1.5
Hexane	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
	100	148.0	13.5	0.0
1-Hexene	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
	100	140.7	13.7	1.3
Heptane	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
	100	164.0	13.7	0.0
1-Heptene	45	145.5	14.8	1.4
	60	148.4	14.6	1.3
	100	156.8	13.9	0.9
Decane	25	195.8	15.8	0.0
Cyclopentane	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
	100	105.2	14.9	0.0
Cyclohexane	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
	100	119.4	14.9	0.0
Ethylcyclohexane	25	143.3	16.2	0.7
Butylcyclohexane	25	176.4	16.1	0.6
Benzene	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
	100	98.8	17.0	0.0
Ethylbenzene	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/°C	V/cm^{3}mol^{-1}	Nonpolar, δ_λ/MPa$^{1/2}$	Polar, δ_τ/MPa$^{1/2}$
Butylbenzene	25	156.8	18.0	0.3
p-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.

$$^{ij}A = ({}^i\delta_\tau - {}^j\delta_\lambda)^2 + ({}^i\delta_\tau - {}^j\delta_\tau)^2 - 2\ {}^{ij}\psi \qquad (52a)$$

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

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

It follows from this form of the dependence of $^{ij}\psi$ on δ_τ that Equation 52a can be rewritten as[25]

$$^{ij}A = ({}^i\delta_\lambda - {}^j\delta_\lambda)^2 + {}^{ij}b\ ({}^i\delta_\tau - {}^j\delta_\tau)^2 \qquad (52b)$$

Values found for the induction cohesive pressure correction factor ^{ij}b 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

$$^{ij}\Psi = {}^i\delta_i\,{}^j\delta_d + {}^i\delta_d\,{}^j\delta_i + {}^i\delta_o\,{}^j\delta_o \qquad (53)$$

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

Liquid	t/°C	V/cm^{3}mol^{-1}	Nonpolar, δ_λ/MPa$^{1/2}$	Polar, δ_τ/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
N,N-Dimethylacetamide	0	90.7	17.6	16.1
	25	93.2	16.9	14.8
	45	95.3	16.5	14.2
N,N-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
Ethyl butyl ketone	25	139.8	16.1	7.4
	60	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/°C	V/cm^{3}mol^{-1}	Nonpolar, δ_λ/MPa$^{1/2}$	Polar, δ_τ/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
N-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.

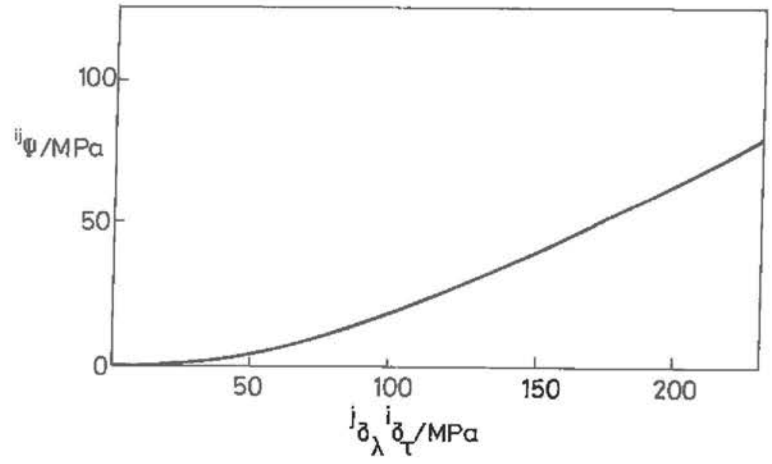


FIGURE 4. Contribution of induction interactions to interchange cohesive pressure at 25°C. (Adapted from Blanks, R. F. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 3, 1, 1964.)

TABLE 10
Values of Induction Cohesive Pressure Correction Factor (${}^{ij}b$)

Component *i* (interacting with liquid *j*)	${}^{ij}b$	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 *j*[a]	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 (*mo*dified *s*eparation of *c*ohesive *e*nergy *d*ensity) 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 Thomas[157] 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 ${}^{ij}\beta$ for solute-solvent interactions so Equation 52b simplified to

$$ {}^{ij}A = ({}^{i}\delta_d - {}^{j}\delta_d)^2 + {}^{j}\delta_\tau^{\,2} - {}^{ij}\beta \qquad (52c)$$

Seidel and Bittrich[116] 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

Hansen[9-30] 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:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{54}$$

These parameters are listed in Table 11. Hansen's total cohesion parameter, δ_t, 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 equation[117] 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. Burrell[50] 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 Dickey[118] 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

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

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

$${}^{ij}A = ({}^i\delta_d - {}^j\delta_d)^2 + 0.25\,[({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2] \tag{56}$$

The distance ${}^{ij}R$ in Equation 55 can be compared with the radius ${}^jR$ of a solute sphere of solubility, and if ${}^{ij}R < {}^jR$ 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/cm^3 mol^{-1}	$\delta/\text{MPa}^{1/2}$ 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[c]	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[d]	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

	[illegible]	18.0	0.0	0.6	18.0
Tetrahydronaphthalene, tetralin	136.0[a]	19.6[d]	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
Halohydrocarbons					
Chloromethane, methyl chloride	55.4	15.3[a]	6.1	3.9	17.0
Dichloromethane, methylene dichloride	63.9	18.2	6.3	6.1	20.3
Bromochloromethane	65.0	17.4	5.7	3.5	18.6
Chlorodifluoromethane, Freon 22	72.9	12.3	6.3	5.7	14.9
Dichlorofluoromethane, Freon 21	75.4	15.8	3.1	5.7	17.1
Bromoethane, ethyl bromide	76.9	15.8	3.1	5.7	17.0
1,1-Dichloroethylene	79.0	17.0	6.8	4.5	18.8
1,2-Dichloroethane, ethylene dichloride	79.4	19.0[a]	7.4	4.1	20.9
Diiodomethane, methylene diiodide	80.5	17.8	3.9	5.5	19.0
Trichloromethane, chloroform	80.7	17.8	3.1	5.7	19.0
1,1-Dichloroethane, ethylidene chloride	84.8	16.6	8.2	0.4	18.5
1,1-Dibromoethane, ethylidene bromide	—	18.4[f]	5.1[f]	6.5[f]	20.2[f]
1,2-Dibromoethane, ethylene dibromide	87.0	19.0	6.8	12.1	23.9
Tribromomethane, bromoform	87.5	21.5[a]	4.1	6.1	22.7[a]
1-Chloropropane, propyl chloride	88.1	16.1	7.8	2.0	17.8
Trichloroethylene	90.2	18.0	3.1	5.3	19.0
Dichlorodifluoromethane, Freon 12	92.3	12.3	2.0	0.0	12.5
Trichlorofluoromethane, Freon 11	92.8	15.3	2.1	0.0	15.4
Bromotrifluoromethane	97.0	9.6	2.5	0.0	9.9
Tetrachloromethane, carbon tetrachloride	97.1	17.8	0.0	0.6	17.8
1,1,1-Trichloroethane	100.4	17.0	4.3	2.1	17.7
Tetrachloroethylene, perchloroethylene	101.1	19.0	6.5	2.9[a]	20.3
Chlorobenzene	102.1	19.0	4.3	2.0	19.6
Butyl chloride, 1-chlorobutane	104.9	16.4	5.5	2.1	17.4
1,1,2,2-Tetrachloroethane	105.2[a]	18.8	5.1	9.4	21.6
Bromobenzene	105.3	20.5	5.5	4.1	21.7
o-Dichlorobenzene	112.8	19.2	6.3	3.3	20.5
Benzyl chloride	115.0	18.8[a]	7.2	2.7	20.3
1,1,2,2-Tetrabromoethane[c]	116.8	22.7	5.1	8.2	24.7
1,2-Dichlorotetrafluoroethane, Freon 114[c]	117.0	12.7	1.8	0.0	12.8
1,1,2-Trichlorotrifluoroethane, Freon 113	119.2	14.7	1.6	0.0	14.7
Cyclohexyl chloride	121.3	17.4	5.5	2.1	18.4
1-Bromonaphthalene	140.0	20.3	3.1	4.1	20.9
Trichlorobiphenyl[d]	187.0	19.2	5.3	4.1	20.3
Perfluor(methylcyclohexane)	196.0	12.5	0.0	0.0	12.5
Perfluor(dimethylcyclohexane[e])	217.4	12.5	0.0	0.0	12.5
Perfluoroheptane	227.3	12.5	0.0	0.0	12.1

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

Liquid	$V/cm^3\ mol^{-1}$	$\delta/MPa^{1/2}$			
		δ_d	δ_p	δ_h	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-(*m*-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 isoamyl 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-furancarboxyaldehyde	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
Isoamyl 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	$V/cm^3\ mol^{-1}$	$\delta/MPa^{1/2}$ δ_d	δ_p	δ_h	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
Nitromethane	54.3	15.8	18.8	5.1	25.1
Nitroethane	71.5	16.0	15.5	4.5	22.7
2-Nitropropane	86.9	16.2	12.1	4.1	20.6
Nitrobenzene	102.7	20.0	8.6	4.1	22.2
Ethanolamine, 2-aminoethanol	60.2	17.2	15.6	21.3	31.5
Ethylenediamine	67.3	16.6	8.8	17.0	25.3
1,1-Dimethylhydrazine[c]	76.0	15.3	5.9	11.0	19.8
2-Pyrrolidone	76.4	19.4	17.4	11.3	28.4
Pyridine	80.9	19.0	8.8	5.9	21.8
Propylamine	83.0	17.0	4.9	8.6	19.7
Morpholine	87.1	18.8	4.9	9.2	21.5
Aniline	91.5	19.4	5.1	10.2	22.6
N-Methyl-2-pyrrolidone	96.5	18.0	12.3	7.2	22.9
Butylamine, 1-butanamine	99.0	16.2[a]	4.5[a]	8.0[a]	18.6
Diethylamine	103.2	14.9	2.3	6.1	16.3
Diethylenetriamine	108.0	16.8	13.3	14.3	25.8
Cyclohexylamine	115.2	17.4	3.1	6.6	18.9
Quinoline	118.0	19.4	7.0	7.6	22.0
Dipropylamine	136.9	15.3	1.4	4.1	15.9
Formamide	39.8	17.2	26.2	19.0	36.6
N,N-Dimethylformamide	77.0	17.4	13.7	11.3	24.8
N,N-Dimethylacetamide	92.5	16.8	11.5	10.2	22.7
Tetramethylurea	120.4	16.8	8.2	11.1	21.7
Hexamethyl phosphoramide[c]	175.7	23.2	8.6	11.3	23.2

[illegible]	120.4	16.8	8.2	11.1	21.7
Hexamethyl phosphoramide[c]	175.7	23.2	8.6	11.3	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
Ethanethiol[c], 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[a]	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®	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	$V/cm^3\ mol^{-1}$	$\delta/MPa^{1/2}$ 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[d]	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[c]	159	15.1	3.3	8.2	17.5
Oleic acid, 9-octadecenoic acid[d]	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

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
m-Cresol, 3-methylphenol	104.7	18.0	5.1	12.9	22.7
o-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[f]	18.0	15.6[e]	16.0[e]	42.3[e]	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[d] (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.

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

Liquids	$\delta/MPa^{1/2}$		
	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
o-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	$\delta/MPa^{1/2}$		
	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]
N,N-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	$\delta/MPa^{1/2}$		
	δ_d	δ_p	δ_h
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	$\delta/MPa^{1/2}$		
	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
o-Xylene, 1,2-dimethylbenzene	17.8	1.0	3.1
Refrigerants			
R11, CCl_3F, trichlorofluoromethane	15.3	2.1	0.0
R12, CCl_2F_2 dichlorodifluoromethane	12.3	2.1	0.0
R13, $CClF_3$ chlorotrifluoromethane	4.9	1.8	0.0
R21, CCl_2FH, dichlorofluoromethane	15.8	3.1	5.7
R22, $CClF_2H$, chlorodifluoromethane	12.3	6.3	5.7
R40, $CClH_3$, chloromethane	15.6	6.1	3.9
R113, $C_2Cl_3F_3$, 1,1,2-trichloro-1,2,2-trifluoroethane	14.7	1.6	0.0
R114, $C_2Cl_2F_4$, 1,2-dichlorotetrafluoroethane	12.7	1.8	0.0
R115, C_2ClF_5, chloropentafluoroethane	9.8	1.8	0.0
R13B1, $CBrF_3$, bromotrifluoromethane	9.6	2.5	0.0
R142b, $C_2ClF_2H_3$, chlorodifluoroethane	11.9	5.7	4.1
R152a, $C_2F_2H_4$ difluoroethane	9.2	10.2	5.7
C318, c-C_4F_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.

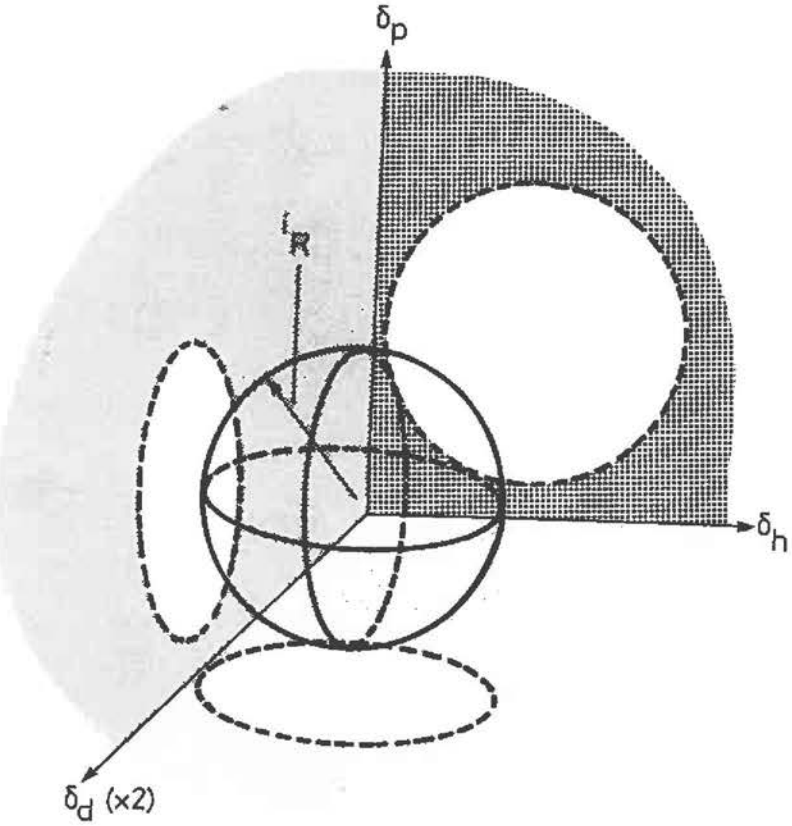


FIGURE 5. Representation of a Hansen parameter solubility sphere and its projections on three axial planes. (Adapted from Beerbower, A. and Dickey, J. R., *Am. Soc. Lubric. Eng. Trans.* 12, 1, 1969.)

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:

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

Hansen[155] has also defined the *relative energy difference* as the ratio $^{ij}R/^{j}R$, 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

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

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

	$\delta/MPa^{1/2}$				
	δ_d	δ_p	δ_h	δ_t	^jR
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[a]	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

[a] 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 ^ib is a Hansen weighting factor, a property of component i, with values (Table 13) comparable to those of ^{ij}b in Table 10. These values have been interpreted physically[124] 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_t values are considerably lower than and inconsistent with those previously reported, which appear to be appropriate for solutions of *water in organic liquids*. (Grunwald[127] 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 Tawn[128] 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 Hansen[155] 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	^ib
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
tert-Butanol	0.20
1-Pentanol	0.19
1-Hexanol	0.28
sec-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	
Diolein	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

Teas[129] showed that for several polymer-liquid systems it is possible to use *fractional cohesive pressures* plotted on a triangular chart to represent miscibility limits:

$$U_d/U = \delta_d^2/\delta_t^2;\ U_p/U = \delta_p^2/\delta_t^2;\ U_h/U = \delta^2{}_h/\delta_t^2 \quad (59)$$

where

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

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

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

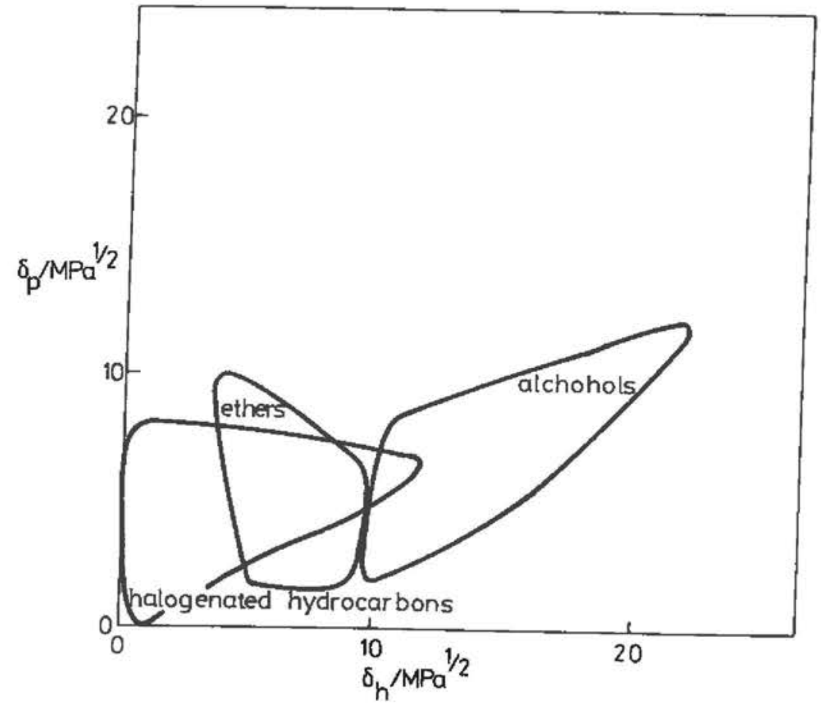


FIGURE 6. Hansen paremeter $\delta_p - \delta_h$ locations for major liquid groups: (A) ethers, halogenated hydrocarbons, and alcohols; (B) esters, aromatic hydrocarbons, ketones, and phenols; (C) aldehydes, polyhydric alcohols, unionized acids, and alkanes; and (D) proton donors (acids, phenols, amines, 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 Teas[119] 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 $(-U_h)$,

$$-U = -U_d - U_p - U_h \tag{63}$$

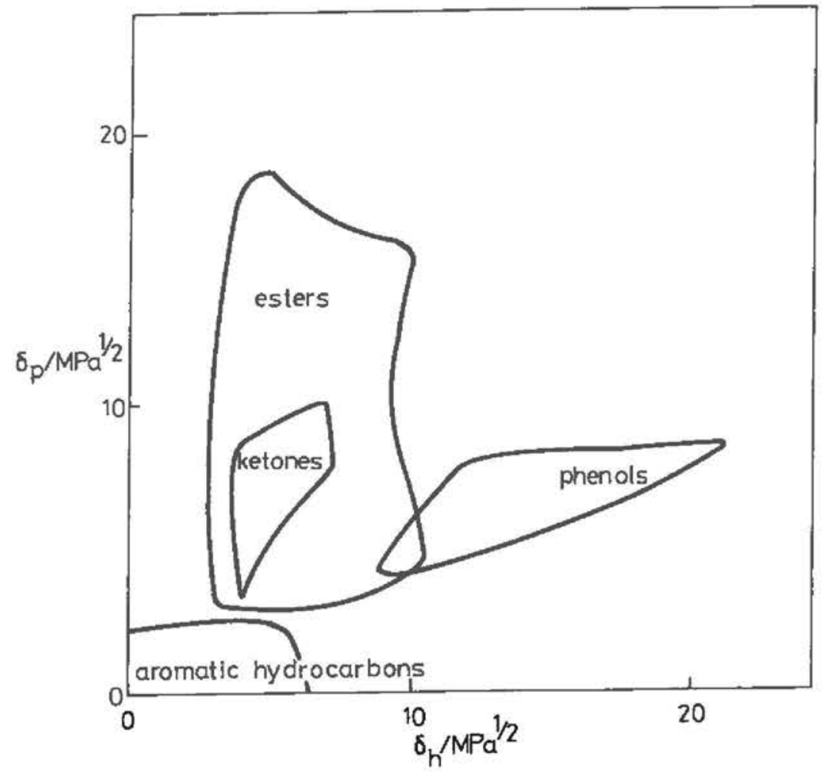


FIGURE 6B.

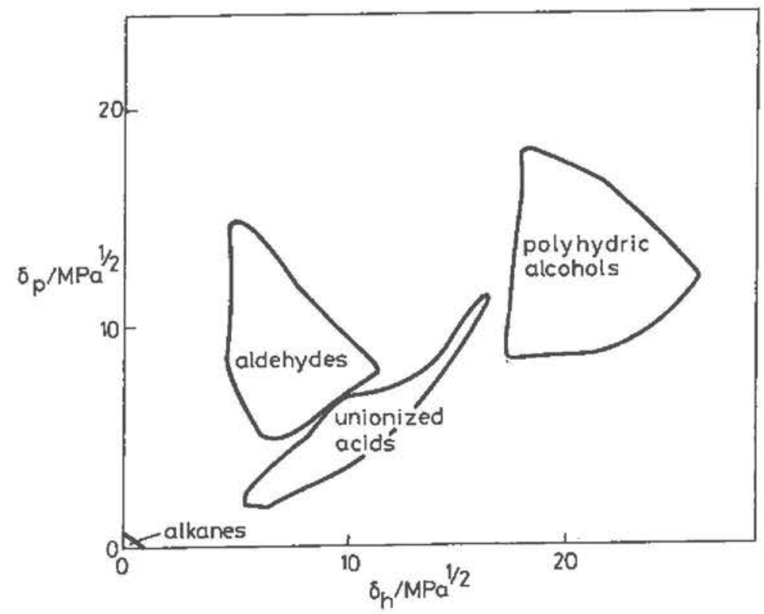


FIGURE 6C.

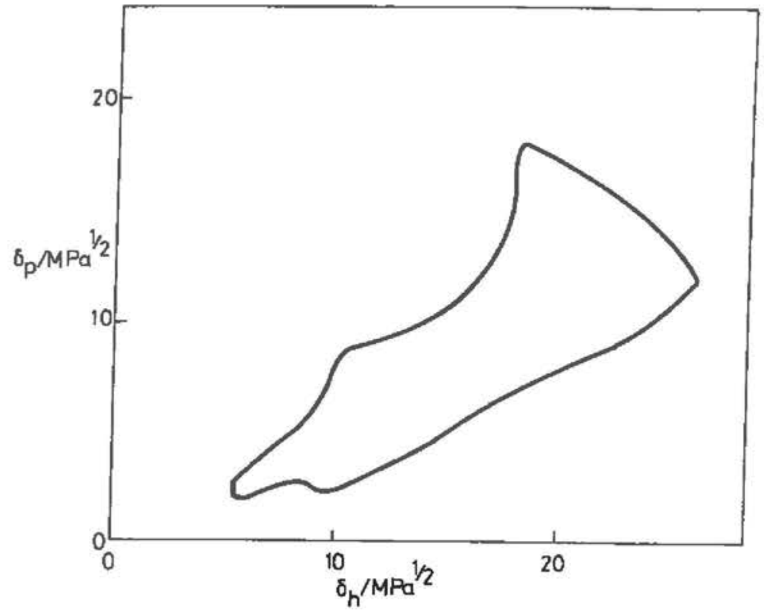


FIGURE 6D.

TABLE 14
Hansen Parameters for Water

δ/MPa$^{1/2}$						
δ_d	δ_p	δ_h	δ_t	^jR	Source	Ref.
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

$$-U/V = -U_d/V - U_p/V - U_h/V \tag{64}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{65}$$

as seen in Equation 54, and

$$^{ij}A = (^i\delta_d{}^i\delta_d - {}^j\delta_d)^2 + (^i\delta_p - {}^j\delta_p)^2 + (^i\delta_h - {}^j\delta_h)^2 \tag{66}$$

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	δ_t/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_ξ to represent the cohesive pressure due to association or hydrogen bonding:

$$\delta_t^2 = \delta_\lambda^2 + \delta_\tau^2 + \delta_\xi^2 \quad (67)$$

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

TABLE 16
Fractional Hansen Parameters of Liquids, Plasticizers and Oils

Compound	δ_t/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
m-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	δ_t/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
o-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-Dichloroetetrafluoroethane, 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)
N,N-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	δ_t/MPa$^{1/2}$	$100f_d$	$100f_p$	$100f_h$
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	δ_t/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.

$$\delta_\lambda^2 \approx \delta_d^2 \tag{68}$$

$$\delta_\tau^2 \approx \delta_p^2 \approx \delta_o^2 + 2\delta_i\delta_d \tag{69}$$

$$\delta_\xi^2 \approx \delta_h^2 \approx 2\delta_a\delta_b \tag{70}$$

The association parameter δ_ξ 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:

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

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

Hoy[126] 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	$\delta/MPa^{1/2}$		
	δ_t	δ_f	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
o-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
N,N-Dimethylacetamide	22.1	17.4	13.6
N,N-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
p-Xylene	18.1	18.0	0.8

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

1. Evaluation of the total cohesion parameter or Hildebrand parameter δ_t 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

$$\log\alpha = 3.39066\, T_b/T_c - 0.15848 - \log (M/\rho) \tag{71}$$

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

$$(T_b/T_c = 0.567 + \Sigma_z\Delta_T - (\Sigma_z\Delta_T)^2 \tag{72}$$

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

TABLE 17
Lyderson Group Constants

Group, z	$10^2\ {}^z\Delta_T$ Aliphatic	$10^2\ {}^z\Delta_T$ Cyclic	$10^2\ {}^z\Delta_T^P$
$-CH_3$	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
$-(CO_2O)$	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	$10^2\ {}^z\Delta_T$ Aliphatic	Cyclic	$10^2\ {}^z\Delta_T^p$
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

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

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:

$$\delta_p = \delta_t\,[\Sigma_z{}^zF_p/(\alpha\Sigma_z\,{}^zF)]^{1/2} \tag{74}$$

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 Eisen[138] (Table 19). Stekol'shchikov, Krivtsova, and Ratner[139] 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 Mogensen[142] 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_d	δ_p	δ_h	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
N-(2-Aminoethyl)ethanolamine	104.2	1.025	13.9	12.8	20.8	28.1
N-(2-Aminoethyl)piperazine	129.2	0.978	15.6	11.7	9.0	21.4
N-(3-Aminopropyl)morpholine	144.2	0.981	16.1	10.2	7.3	20.4
Amyl alcohol, see 1-Pentanol						
sec-Amyl alcohol, see 2-Pentanol	88.2	0.815	14.5	9.1	13.9	22.0
prim. active Amyl alcohol, 2-methyl-1-butanol						
tert-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
N,N-(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, *sec*-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
o-Bromostyrene	183.1	1.408	17.7	9.6	0.0	20.1
o-Bromotoluene	171.0	1.437	17.9	8.8	0.0	20.0
p-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, *sec*-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
cis-2-Butene	56.1	0.614	12.9	3.8	5.8	14.6
trans-2-Butene	56.1	0.597	13.1	3.6	4.2	14.2
cis-1-Butenyl methyl ether	86.1	0.770	14.2	6.4	6.2	16.8
trans-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
sec-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}	ρ/g cm^{-3}	δ/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
o-Butyltoluene	148.2	0.865	16.6	6.1	0.0	17.7
m-Butyltoluene	148.2	0.853	16.5	6.0	0.0	17.5
p-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, *sec*-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
o-Chlorostyrene	138.6	1.093	17.1	9.4	0.0	19.6
p-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	ρ/g cm⁻³	δ/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-Cyclohexyldodecane	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-Cyclopentyloctane	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, *sec*-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
o-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
N,N-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
o-Dichlorobenzene	147.0	0.298	18.0	9.8	0.0	20.5
m-Dichlorobenzene	147.0	0.281	17.6	9.5	0.0	20.0
p-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	$M/g\ mol^{-1}$	$\rho/g\ cm^{-3}$	$\delta/MPa^{1/2}$			
			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