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

			$\delta/\mathrm{MPa}^{1/2}$			
Liquid	$M/\mathrm{g\ mol}^{-1}$	$\rho/\mathrm{g\ cm}^{-3}$	δ_d	δ_p	δ_h	δ_t
2,3-Dimethyl-1-butene	84.2	0.672	13.9	3.8	3.0	14.7
3,3-Dimethylbutyl acetate	144.2	0.863	14.9	7.1	3.0	16.8
1,3-Dimethylbutylamine	101.2	0.743	14.2	7.3	3.8	16.3
Dimethyl Cellosolve®	90.1	0.862	13.9	7.7	7.7	17.7
1,1-Dimethylcyclohexane	112.2	0.775	15.4	2.6	0.0	15.7
1,1-Dimethylcyclopentane	98.2	0.749	15.1	3.2	0.0	15.4
2,5-Dimethyl-3,4-dihydro-2*H*-pyran-2-carboxyaldehyde	140.2	0.991	13.9	10.5	4.7	18.1
Dimethyl diketone	86.1	0.976	10.6	12.7	11.7	20.3
2,6-Dimethyl-1,4-dioxane	116.2	0.939	15.7	8.3	4.3	18.2
N,*N*-Dimethylethanolamine	89.1	0.882	13.5	8.5	14.0	21.2
N,*N*-Dimethyl-2-ethylhexylamine	157.3	0.764	15.3	3.1	1.6	15.7
2,5-Dimethylfuran	96.1	0.894	15.8	7.0	4.8	17.9
2,2-Dimethylheptane	128.3	0.705	14.9	0.0	0.0	14.9
2,3-Dimethylheptane	128.3	0.721	15.3	0.0	0.0	15.3
2,4-Dimethylheptane	128.3	0.711	15.0	0.0	0.0	15.0
2,5-Dimethylheptane	128.3	0.710	15.1	0.0	0.0	15.1
2,6-Dimethylheptane	128.3	0.704	15.0	0.0	0.0	15.0
3,3-Dimethylheptane	128.3	0.720	15.1	0.0	0.0	15.1
3,4-Dimethylheptane	128.3	0.726	15.4	0.0	0.0	15.4
3,5-Dimethylheptane	128.3	0.718	15.1	0.0	0.0	15.1
4,4-Dimethylheptane	128.3	0.720	15.0	0.0	0.0	15.0
2,6-Dimethyl-4-heptanol	144.3	0.807	14.3	6.7	9.2	18.3
2,6-Dimethyl-4-heptyl acetate	186.3	0.847	14.4	6.1	2.2	15.8
2,2-Dimethylhexane	114.2	0.690	14.5	0.0	0.0	14.5
2,3-Dimethylhexane	114.2	0.707	15.0	0.0	0.0	15.0
2,4-Dimethylhexane	114.2	0.695	14.7	0.0	0.0	14.7
2,5-Dimethylhexane	114.2	0.688	14.6	0.0	0.0	14.6
3,3-Dimethylhexane	114.2	0.705	14.7	0.0	0.0	14.7
3,4-Dimethylhexane	114.2	0.704	14.9	0.0	0.0	14.9
2,8-Dimethyl-6-isobutyl-4-nonanol	228.4	0.822	13.8	5.3	6.9	16.3
Dimethylisopropanolamine	103.2	0.845	12.6	7.7	11.2	18.5
Dimethyl maleate	144.1	1.146	14.5	12.1	11.8	22.3
2,6-Dimethylmorpholine	115.2	0.928	16.4	10.0	2.3	19.3
2,2-Dimethyloctane	142.3	0.719	14.9	0.0	0.0	14.9
2,3-Dimethyloctane	142.3	0.732	15.3	0.0	0.0	15.3
2,4-Dimethyloctane	142.3	0.721	14.9	0.0	0.0	14.9
2,5-Dimethyloctane	142.3	0.731	15.1	0.0	0.0	15.1
2,6-Dimethyloctane	142.3	0.723	15.1	0.0	0.0	15.1
2,7-Dimethyloctane	142.3	0.719	15.0	0.0	0.0	15.0
3,3-Dimethyloctane	142.3	0.734	15.3	0.0	0.0	15.3
3,4-Dimethyloctane	142.3	0.741	15.4	0.0	0.0	15.4
3,5-Dimethyloctane	142.3	0.731	15.2	0.0	0.0	15.2
3,6-Dimethyloctane	142.3	0.731	15.2	0.0	0.0	15.2
4,4-Dimethyloctane	142.3	0.732	15.2	0.0	0.0	15.2
4,5-Dimethyloctane	142.3	0.742	15.4	0.0	0.0	15.4
2,3-Dimethylpentaldehyde	114.2	0.823	14.5	7.7	6.3	17.6
2,2-Dimethylpentane	100.2	0.668	14.1	0.0	0.0	14.1
2,3-Dimethylpentane	100.2	0.690	14.8	0.0	0.0	14.8
2,4-Dimethylpentane	100.2	0.667	14.2	0.0	0.0	14.2
3,3-Dimethylpentane	100.2	0.688	14.5	0.0	0.0	14.5
2,3-Dimethylpentanol	116.2	0.837	14.8	8.2	12.0	20.8
2,3-Dimethylpentenal	112.2	0.837	14.1	8.7	6.7	17.8
Dimethyl phthalate	194.2	0.119	15.9	12.6	9.7	22.5

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
Dimethyl pimelate	188.2	1.034	14.8	9.4	9.6	20.0
2,2-Dimethylpropane	72.2	0.584	12.5	0.0	0.0	12.5
2,5-Dimethyltetrahydrofuran	100.2	0.825	15.6	6.5	0.0	16.9
1,4-Dioxane, diethylene oxide	88.1	1.028	16.3	10.1	7.9	20.7
1,3-Dioxolane	64.1	1.058	14.8	11.3	13.9	23.2
Dipentene	136.2	0.836	16.3	5.8	0.0	17.3
Diphenyl ether	170.2	1.061	17.4	11.2	0.0	20.7
Diphenylmethane	168.2	1.000	17.2	9.4	0.0	19.5
1,1-Dipropoxyethane	146.2	0.825	13.9	6.2	5.1	16.0
Dipropylamine	101.2	0.732	14.0	6.2	5.8	16.3
Dipropylene glycol, Oxybispropanol	134.2	1.016	12.2	10.3	17.4	23.6
Dipropylenetriamine	131.2	0.898	13.2	11.5	10.6	20.5
Dipropyl ketone	114.2	0.811	14.6	7.5	6.9	17.8
2,3-Dithiabutane	94.2	1.055	13.9	13.4	5.4	20.1
Divinyl Carbitol®	158.2	0.964	14.3	9.0	9.4	19.3
Dodecane	170.3	0.744	16.2	0.0	0.0	16.2
1-Dodecanol, lauryl alcohol	186.3	0.829	15.5	6.5	10.8	20.0
2-Dodecanol, 2-dodecyl alcohol	186.3	0.825	13.7	5.8	9.2	17.4
Epichlorohydrin, (chloromethyl)oxirane	92.5	1.168	15.9	12.3	10.5	22.7
3,4-Epoxy-1-butene	70.1	0.869	14.8	9.8	8.6	19.7
Ethanol	46.1	0.785	12.6	11.2	20.0	26.1
2-Ethoxy-3,4-dihydro-1,2-pyran	128.2	0.963	14.8	8.8	4.9	17.9
1-Ethoxyethoxy-2-propanol	148.2	0.950	13.4	8.5	12.8	20.4
3-Ethoxy-4-ethyloctanol	202.3	0.879	14.4	6.4	9.9	18.5
2-Ethoxy-4-methyl-3,4-dihydropyran	142.2	0.927	14.9	8.3	3.7	17.4
5-Ethoxy-3-methylpentanol	146.2	0.894	14.4	8.6	12.5	20.9
2-Ethoxy-4-methyltetrahydropyran	144.2	0.908	15.4	7.4	2.9	17.3
1-Ethoxy-2-propanol	104.2	0.892	13.0	8.5	12.8	20.1
3-Ethoxypropanol	104.2	0.912	14.0	8.7	14.8	22.1
3-Ethoxypropionaldehyde	102.1	0.911	13.5	9.7	10.5	19.7
3-Ethoxypropionic acid	118.1	1.041	16.5	11.5	16.5	26.0
3-Ethoxypropyl acetate	158.2	0.957	14.5	8.2	8.2	18.6
2-Ethoxy-4-propyl-5-ethyl-3,4-dihydropyran	198.3	0.914	14.9	6.8	4.8	17.0
2-Ethoxytetrahydropyran	130.2	0.933	14.9	7.7	4.2	17.3
Ethoxytriglycol	178.2	1.015	13.1	8.8	13.5	20.8
Ethyl acetate	88.1	0.894	13.4	8.6	8.9	18.2
Ethyl acetoacetate	130.1	1.019	13.3	11.1	10.2	20.1
Ethyl acrylate	100.1	0.915	13.3	9.3	7.9	18.0
Ethyl amyl ketone	128.2	0.816	14.5	7.2	5.7	17.2
N-Ethylaniline	121.2	0.957	17.1	10.5	7.7	21.5
Ethylbenzene	106.2	0.862	16.5	7.4	0.0	18.1
Ethyl benzoate	150.2	1.041	15.7	10.6	6.3	19.9
Ethyl bromide, see Bromoethane						
2-Ethyl-1,3-butadiene	82.2	0.713	14.3	5.6	0.0	15.4
2-Ethylbutanol	102.2	0.829	14.4	8.5	13.0	21.2
2-Ethyl-1-butene	84.2	0.684	14.3	3.9	3.1	15.2
2-Ethylbutyl acetate	144.2	0.874	14.6	7.0	5.3	17.0
N-Ethylbutylamine	101.2	0.735	13.9	6.2	5.9	16.3
2-Ethylbutyl Carbitol®	190.3	0.933	13.3	7.4	11.2	18.9
2-Ethylbutyl Cellosolve®	146.2	0.890	13.7	7.3	11.5	19.4
Ethyl butyl ether	102.2	0.745	14.3	4.8	4.5	15.7
2-Ethylbutyl 2-ethylbutyrate	200.3	0.861	14.3	5.8	4.7	16.1
2-Ethylbutyl 2-ethylhexanoate	228.4	0.853	14.7	5.4	4.9	16.5
2-Ethylbutyl hexanoate	200.3	0.863	14.4	5.8	5.5	16.4

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
Ethyl butyl ketone	114.2	0.813	14.2	7.4	6.9	17.4
2-Ethylbutyraldehyde	100.2	0.810	14.0	7.9	7.2	17.6
Ethyl butyrate	116.2	0.874	13.8	7.6	6.4	17.0
2-Ethylbutyric acid	116.2	0.919	17.4	9.3	12.9	23.5
2-Ethylcrotonaldehyde	98.2	0.852	14.4	9.5	7.6	18.9
Ethyl crotonate	114.1	0.913	14.0	8.8	7.6	18.2
Ethylcyclohexane	112.1	0.783	16.1	2.6	0.0	16.3
N-Ethylcyclohexylamine	127.2	0.842	15.8	7.0	3.0	17.6
Ethylcyclopentane	98.2	0.761	15.9	3.3	0.0	16.2
N-Ethyldiethanolamine	133.2	1.010	13.2	9.5	18.2	24.4
N-Ethyldiisopropanolamine	161.3	0.940	12.5	8.4	14.1	20.6
4-Ethyl-2,6-dimethylmorpholine	136.2	0.876	15.8	6.6	2.1	17.2
3-Ethyl-2,2-dimethylpentane	128.3	0.730	14.9	0.0	0.0	14.9
3-Ethyl-2,3-dimethylpentane	128.3	0.749	15.3	0.0	0.0	15.3
Ethyl 2,5-endomethylene-3-cyclohexanecarboxylate	166.2	1.021	14.7	7.7	10.9	19.8
Ethylene chlorohydrin, 2-chloroethanol	80.5	1.197	12.0	13.3	19.6	26.5
Ethylene cyanohydrin	71.1	1.041	11.1	15.2	24.7	31.0
Ethylenediamine, 1,2-ethanediamine	60.1	0.903	12.6	14.0	16.9	25.3
Ethylene glycol, 1,2-ethanediol	62.1	1.110	10.1	15.1	29.8	34.9
N-Ethylethanolamine	89.1	0.913	14.3	10.5	17.8	25.1
Ethyl ether, diethyl ether	74.1	0.703	13.4	5.3	5.6	15.4
Ethyl 3-ethoxybutyrate	160.2	0.924	14.1	8.0	6.7	17.5
Ethyl 3-ethoxypropionate	146.2	0.943	14.3	8.5	8.0	18.4
3-Ethylheptane	128.3	0.722	15.4	0.0	0.0	15.4
4-Ethylheptane	128.3	0.725	15.5	0.0	0.0	15.5
5-Ethyl-3-hepten-2-one	140.2	0.841	15.0	7.8	6.6	18.1
2-Ethylhexaldehyde	128.2	0.815	14.3	7.1	6.5	17.2
3-Ethylhexane	114.2	0.708	15.2	0.0	0.0	15.2
2-Ethylhexanoic acid	144.2	0.902	17.4	8.3	11.6	22.5
2-Ethylhexanol	130.2	0.829	15.1	7.7	12.0	20.8
2-Ethyl-1-hexene	112.2	0.722	15.0	3.6	0.0	15.5
2-Ethylhexyl acetate	172.3	0.867	14.8	6.3	5.4	17.0
2-Ethylhexyl acrylate	184.3	0.881	13.9	6.8	4.5	16.1
2-Ethylhexylamine	129.3	0.784	14.8	6.6	5.9	17.3
2-Ethylhexyl Carbitol®	218.3	0.918	13.9	7.1	10.6	18.9
2-Ethylhexyl Cellosolve®	174.3	0.880	13.7	6.7	10.6	18.5
2-Ethylhexyl chloride	148.7	0.877	15.5	5.4	2.4	16.6
2-Ethylhexyl crotonate	198.3	0.881	15.4	6.7	6.2	17.9
2-Ethylhexyl 2-ethylbutyrate	228.4	0.858	14.1	5.3	4.5	15.7
2-Ethylhexyl-2-ethylhexanoate	256.4	0.855	14.7	5.1	4.7	16.2
2-Ethylhexyl hexanoate	228.4	0.859	14.5	5.4	5.5	16.4
3-(2-Ethylhexoxy)propylamine	187.3	0.843	14.2	6.7	6.8	17.1
2-Ethylhexyl 4-pentenoate	212.3	0.874	14.6	6.3	5.8	17.0
Ethylideneacetone	84.1	0.850	14.3	9.9	9.7	19.9
N-Ethylisopropanolamine	103.2	0.882	13.6	9.5	14.6	22.1
Ethyl isopropenyl ether	86.13	0.764	14.1	6.9	2.7	15.9
Ethyl isopropyl ether	100.2	0.806	15.3	5.1	6.2	17.3
N-Ethyl-α-methylbenzylamine	149.2	0.906	15.4	8.8	4.3	18.2
2-Ethyl-2-methyl-1,3-dioxolane	116.2	0.932	15.4	8.5	0.0	17.6
3-Ethyl-2-methylheptane	142.3	0.741	15.4	0.0	0.0	15.4
3-Ethyl-3-methylheptane	142.3	0.745	15.4	0.0	0.0	15.4
3-Ethyl-4-methylheptane	142.3	0.748	15.6	0.0	0.0	15.6
4-Ethyl-2-methylheptane	142.3	0.731	15.2	0.0	0.0	15.2

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
4-Ethyl-3-methylheptane	142.3	0.748	15.6	0.0	0.0	15.6
4-Ethyl-4-methylheptane	142.3	0.747	15.6	0.0	0.0	15.6
5-Ethyl-2-methylheptane	142.3	0.731	15.1	0.0	0.0	15.1
5-Ethyl-3-methylheptane	142.3	0.738	15.3	0.0	0.0	15.3
3-Ethyl-2-methylhexane	128.3	0.726	15.2	0.0	0.0	15.2
3-Ethyl-3-methylhexane	128.3	0.736	15.2	0.0	0.0	15.2
4-Ethyl-2-methylhexane	128.3	0.718	15.0	0.0	0.0	15.0
4-Ethyl-3-methylhexane	128.3	0.737	15.4	0.0	0.0	15.4
3-Ethyl-2-methylpentane	114.2	0.714	15.0	0.0	0.0	15.0
3-Ethyl-3-methylpentane	114.2	0.722	14.9	0.0	0.0	14.9
2-Ethyl-3-methyl-1,5-pentanediol	146.2	0.962	14.2	10.7	16.9	24.5
5-Ethyl-2-methylpiperidine	127.2	0.834	15.7	6.9	1.6	17.2
7-Ethyl-2-methyl-4-undecanol	214.4	0.831	14.3	5.6	8.2	17.4
N-Ethylmorpholine	115.2	0.908	16.6	7.6	0.7	18.3
5-Ethyl-2-nonanone	170.3	0.838	15.1	6.3	6.3	17.5
5-Ethyl-2-nonanol	172.3	0.831	14.3	6.1	9.6	18.3
3-Ethyloctane	142.3	0.735	15.8	0.0	0.0	15.8
4-Ethyloctane	142.3	0.735	15.8	0.0	0.0	15.8
4-Ethyloctanol	158.3	0.834	14.9	7.0	11.0	19.8
3-Ethylpentane	100.2	0.693	15.0	0.0	0.0	15.0
2-Ethyl-1,5-pentanediol	132.2	0.964	13.8	10.8	18.9	25.8
Ethyl propionate	102.1	0.884	14.0	8.1	7.8	17.9
2-Ethyl-3-propylacrolein	126.2	0.846	14.9	8.4	6.6	18.3
2-Ethyl-3-propylacrylic acid	142.2	0.943	18.9	10.1	12.9	25.1
2-Ethyl-2-propylhexanol	172.3	0.850	13.9	6.6	9.7	18.2
Ethyl propyl ketone	100.2	0.811	13.9	7.9	7.3	17.6
3-Ethyl-4-propyltetrahydropyran	156.3	0.874	16.9	5.2	0.0	17.6
m-Ethylstyrene	132.2	0.889	16.8	7.7	0.0	18.5
m-Ethyltoluene	120.2	0.859	16.4	6.7	1.5	17.8
o-Ethyltoluene	120.2	0.875	16.8	6.9	0.0	18.1
p-Ethyltoluene	120.2	0.859	16.4	6.6	2.1	17.8
Fluorobenzene	96.1	1.015	15.4	9.0	5.2	18.6
2-Formyl-3,4-dihydro-2H-pyran	112.1	1.070	13.8	12.0	9.6	20.6
Glycerol, 1,2,3-propanetriol	92.1	1.258	9.3	15.4	31.4	36.2
Glycerol triacetate	218.2	1.153	14.9	11.6	11.2	22.0
Glycol diacetate	146.1	1.099	14.4	11.2	10.6	21.1
Glycol dipropionate	174.2	1.042	14.1	9.7	9.2	19.4
Heptane	100.2	0.679	15.3	0.0	0.0	15.3
2,4-Heptanediol	132.2	0.926	13.4	9.9	16.8	23.7
1-Heptanol	116.2	0.819	15.1	8.0	13.0	21.5
2-Heptanol	116.2	0.813	14.6	7.4	11.7	20.1
3-Heptanol	116.2	0.817	14.6	7.5	11.8	20.2
1-Heptene	98.2	0.692	14.6	3.6	2.7	15.3
cis-2-Heptene	98.2	0.703	15.0	3.4	2.3	15.6
trans-2-Heptene	98.2	0.696	14.9	3.1	2.9	15.5
cis-3-Heptene	98.2	0.697	14.8	3.3	2.5	15.4
trans-3-Heptene	98.2	0.693	14.8	3.1	2.3	15.3
3-Hepten-2-one	112.2	0.842	15.5	9.0	6.4	19.0
2-Heptyl acetate	158.2	0.857	14.6	6.6	4.9	16.8
3-Heptyl acetate	158.2	0.860	14.5	6.6	5.0	16.7
Heptylbenzene	176.3	0.851	16.5	5.6	0.0	17.4
3-Heptyl Carbitol®	204.3	0.924	13.4	7.2	10.7	18.6
3-Heptyl Cellosolve®	160.3	0.880	13.3	6.9	10.7	18.4
2,4-Hexadienal	96.1	0.888	15.1	10.4	11.2	21.5
Hexaldehyde	100.2	0.809	14.2	7.9	8.2	18.2

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

			δ/MPa$^{1/2}$			
Liquid	M/g mol^{-1}	ρ/g cm^{-3}	δ_d	δ_p	δ_h	δ_t
Hexane	86.2	0.654	14.9	0.0	0.0	14.9
2,5-Hexandeiol	118.2	0.957	14.2	10.7	19.3	26.2
2,5-Hexanedione	114.1	0.967	13.6	11.6	11.6	21.1
Hexanoic acid	116.2	0.923	17.2	9.2	13.8	23.9
1-Hexanol	102.2	0.816	15.0	8.5	13.7	22.0
2-Hexanol	102.2	0.810	14.4	7.9	12.3	20.5
3-Hexanol	102.2	0.814	13.5	7.7	11.6	19.4
1-Hexene	84.2	0.668	14.4	3.9	0.0	15.0
cis-2-Hexene	84.2	0.681	14.6	3.5	3.1	15.3
trans-2-Hexene	84.2	0.673	14.6	3.3	2.9	15.2
cis-3-Hexene	84.2	0.674	14.4	3.5	3.4	15.2
trans-3-Hexene	84.2	0.671	14.5	3.3	3.2	15.2
Hexyl acetate	144.2	0.869	14.9	7.0	6.4	17.7
Hexyl acrylate	156.2	0.883	14.7	7.5	6.6	17.8
Hexylamine, 1-hexanamine	101.2	0.762	14.2	7.1	6.9	17.3
Hexylene glycol	118.2	0.918	12.5	11.4	16.8	23.1
Hexylene glycol diacetate	202.3	0.994	13.4	8.7	7.0	17.4
Hexyl Carbitol®	190.3	0.929	13.9	7.5	12.0	19.8
Hexyl Cellosolve®	146.2	0.883	13.8	7.2	12.1	19.7
Hexyl chloride, 1-chlorohexane	120.6	0.873	15.6	6.0	4.0	17.2
Hexyl 2-ethylbutyrate	200.3	0.856	14.3	5.7	5.2	16.2
Hexyl ethyl Carbitol®	218.3	0.881	14.3	6.1	7.2	17.1
Hexyl 2-ethylhexanoate	228.4	0.858	13.8	5.2	5.2	15.6
Hexyl hexanoate	200.3	0.858	14.7	5.8	6.1	17.0
N-(2-Hydroxyethyl)morpholine	131.2	1.068	15.3	8.7	13.8	22.4
N-(2-Hydroxyethyl)piperidine	130.2	1.056	15.0	11.0	15.3	24.1
N-(2-Hydroxyethyl)propylenediamine	118.2	0.988	15.0	12.3	19.2	27.3
Isoamyl alcohol, 3-methyl-1-butanol	88.2	0.806	15.2	9.3	14.1	22.7
sec-Isoamyl alcohol, 3-methyl-2-butanol	88.2	0.813	14.0	8.4	12.4	20.5
Isobutyl acetate	116.2	0.866	14.5	7.8	5.1	17.2
Isobutyl acrylate	128.2	0.884	14.1	8.4	5.7	17.4
Isobutanol, 2-methyl-1-propanol	74.1	0.798	14.4	9.8	15.0	23.0
Isobutyl benzene	134.2	0.848	15.7	6.3	0.0	16.9
Isobutyl Cellosolve®	118.2	0.887	13.9	7.6	12.6	20.2
Isobutylene oxide	72.1	0.801	15.7	8.4	1.3	17.8
Isobutyl heptyl ketone	184.3	0.813	14.7	6.0	3.6	16.3
Isobutyl isobutyrate	144.2	0.849	14.2	7.0	0.0	15.8
Isobutyraldehyde	72.1	0.784	13.1	9.0	8.4	17.9
Isobutyric acid	88.1	0.943	15.4	9.9	16.2	24.5
Isobutyronitrile	69.1	0.765	13.3	10.6	10.6	20.1
Isodecanol	158.3	0.835	14.4	6.9	10.7	19.3
Isooctanol	130.2	0.827	14.4	7.3	12.9	20.7
Isophorone	138.2	0.917	16.4	9.4	3.2	19.2
Isoprene, 2-methyl-1,3-butadiene	68.1	0.675	13.7	5.8	4.0	15.3
Isopropyl acetate	102.1	0.866	14.3	8.4	5.7	17.6
Isopropyl acetoacetate	144.2	0.984	13.4	10.4	8.5	19.0
Isopropyl alcohol, see 2-propanol						
Isopropylamine, see 2-propanamine	59.1	0.681	12.6	8.6	7.0	16.8
Isopropylbenzene	120.2	0.857	16.2	6.9	0.0	17.6
Isopropyl benzoate	164.2	1.005	15.6	10.0	3.9	18.9
Isopropylcyclohexane	126.2	0.797	16.0	2.5	0.0	16.2
Isopropylcyclopentane	112.2	0.771	15.6	3.1	0.0	15.9
N-Isopropyldiisopropanolamine	175.3	0.935	12.7	8.2	13.2	20.1
Isopropyl ether, 2,2′-oxybispropane	102.2	0.718	13.6	4.7	1.5	14.4

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
N-Isopropylisopropanolamine	117.2	0.868	13.5	9.0	12.8	20.7
4-Isopropylheptane	142.3	1.056	15.2	0.0	0.0	15.2
Isopropyl 6-methyl-3-cyclohexenecarboxylate	182.3	0.939	15.4	7.9	0.0	17.3
N-Isopropylmorpholine	129.2	0.909	16.4	7.1	0.0	17.9
Lauryl alcohol, see 1-Dodecanol						
Mesityl oxide	98.2	0.854	14.7	9.6	6.6	18.8
Methacryladehyde	70.1	0.841	12.5	10.7	8.8	18.7
Methacrylic acid	86.1	1.009	17.0	13.0	16.2	26.8
Methallyl cyanide	81.1	0.829	13.9	11.5	10.5	20.9
Methanol	32.0	0.786	11.6	13.0	24.0	29.7
1-Methoxy-1,3-butadiene	84.1	0.826	14.4	8.0	8.2	18.4
3-Methoxybutanol	104.2	0.917	14.1	8.8	14.3	22.0
3-Methoxybutyl acetate	146.2	0.949	14.3	8.6	7.5	18.3
3-Methoxybutyraldehyde	102.1	0.921	13.7	9.9	9.9	19.6
4-Methoxy-2,6-dipropyl-1,3-dioxane	202.3	0.929	14.9	7.3	5.3	17.4
4-Methoxy-4-methyl-2-pentanone	130.2	0.903	13.4	8.8	6.3	17.2
3-Methoxypropionitrile	85.1	0.934	13.7	12.0	14.5	23.3
Methoxytriglycol	164.2	1.043	13.4	9.4	14.8	22.0
Methyl acetate	74.1	0.927	13.3	9.5	10.4	19.4
Methyl acetoacetate	116.1	1.071	13.6	12.2	12.0	21.8
Methyl acrylate	86.1	0.950	13.2	10.2	9.4	19.2
Methylamyl alcohol	102.2	0.803	13.1	7.6	10.5	18.4
Methyl amyl ketone	114.2	0.811	15.1	7.6	7.2	18.4
Methyl benzoate	136.2	1.081	15.9	11.5	7.2	20.8
α-Methylbenzylamine	121.2	0.948	16.1	11.1	5.8	20.4
α-Methylbenzyl Cellosolve®	166.2	1.034	13.7	9.5	11.9	20.5
α-Methylbenzyldimethylamine	149.2	0.899	15.9	7.3	0.0	17.5
2-Methyl-1,3-butadiene, see Isoprene						
2-Methylbutane	72.2	0.614	13.8	0.0	0.0	13.8
2-Methyl-1-butene	70.1	0.645	13.6	4.1	3.7	14.7
2-Methyl-2-butene	70.1	0.657	14.2	4.1	3.8	15.2
3-Methyl-1-butene	70.1	0.621	12.7	3.8	3.7	13.7
N-Methylbutylamine	87.2	0.728	14.2	6.7	6.6	17.0
Methyl butyl ketone	100.2	0.806	14.1	7.9	7.1	17.7
Methyl *sec*-butyl ketone	100.2	0.808	14.1	8.0	6.2	17.4
Methyl *tert*-butyl ketone	100.2	0.801	14.1	8.2	4.1	16.8
3-Methylbutyraldehyde	86.1	0.795	13.6	8.5	7.5	17.7
Methyl Carbitol®	120.2	1.015	13.4	9.6	15.8	22.8
Methyl Carbitol acetate	162.2	1.034	14.6	9.6	10.3	20.3
Methyl Cellosolve®	76.1	0.960	13.0	10.0	17.4	23.9
Methyl Cellosolve acetate	118.1	0.999	14.7	9.8	9.9	20.3
Methyl chloroform, see 1,1,1-Trichloroethane						
4-Methylcyclohexylmethylamine	127.2	0.888	16.2	8.0	5.1	18.8
Methylcyclopentane	84.2	0.743	15.7	3.5	0.0	16.0
N-Methyldibutylamine	143.3	0.755	15.2	3.2	2.9	15.8
N-Methyldiethanolamine	119.2	1.036	12.8	11.0	20.1	26.2
4-Methyl-3,4-dihydropyran	98.2	0.890	15.5	7.9	2.5	17.5
2,5-*endo*Methylenecyclohexylmethylamine	125.2	0.936	16.5	8.2	6.1	19.4
2,5-*endo*Methylenecyclohexane-1-methanol	140.3	0.986	16.4	9.0	11.1	21.8
2,5-*endo*Methylene-3-cyclohexenyl acetate	152.2	1.045	16.0	9.2	5.4	19.3
2,5-*endo*Methylenecyclohexyl acetate	154.2	1.022	16.7	8.2	5.1	19.3
Methylene dichloride, see Dichloromethane						
N-Methylethanolamine	75.1	0.936	14.1	11.4	20.0	27.0
Methyl ethyl Carbitol®	148.2	0.918	14.5	7.6	8.6	18.5

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
Methyl ethyl ether	60.1	0.692	13.0	5.7	6.2	15.5
Methyl ethyl ketone	72.1	0.800	14.1	9.3	9.5	19.3
2-Methyl-5-ethylpyridine	121.2	0.916	17.7	7.7	2.5	19.5
2-Methylheptane	114.2	0.693	15.0	0.0	0.0	15.0
3-Methylheptane	114.2	0.700	15.1	0.0	0.0	15.1
4-Methylheptane	114.2	0.699	15.1	0.0	0.0	15.1
2-Methyl-1-heptene	112.2	0.715	14.9	3.6	0.0	15.3
2-Methyl-2-heptene	112.2	0.719	15.3	3.5	0.0	15.7
3-Methyl-1-heptene	112.2	0.706	14.4	3.4	1.3	14.9
3-Methyl-2-heptene	112.2	0.724	15.3	3.5	0.0	15.7
4-Methyl-1-heptene	112.2	0.712	14.6	3.5	0.0	15.0
5-Methyl-1-heptene	112.2	0.711	14.5	3.4	2.0	15.0
cis-5-Methyl-2-heptene	112.2	0.718	15.2	3.2	0.0	15.5
6-Methyl-1-heptene	112.2	0.707	14.6	3.4	2.2	15.2
cis-6-Methyl-2-heptene	112.2	0.713	15.1	3.2	0.0	15.4
Methyl heptyl ketone	142.2	0.821	14.6	6.9	4.6	16.8
2-Methylhexane	100.2	0.673	14.8	0.0	0.0	14.8
3-Methylhexane	100.2	0.682	14.9	0.0	0.0	14.9
5-Methyl-2-hexanol	116.2	0.808	14.9	7.6	11.3	20.2
Methyl hexyl ketone	128.2	0.814	15.1	7.2	6.8	18.0
N-Methylhomopiperazine	114.2	0.922	16.3	8.9	5.6	19.4
Methyl 3-hydroxybutyrate	118.1	1.053	11.9	10.9	14.6	21.8
Methyl isoamyl ketone	114.2	0.807	14.9	7.7	5.8	17.7
Methyl isobutyl ketone	100.2	0.796	14.4	8.1	5.9	17.6
Methyl isocyanate	57.1	0.951	11.2	12.2	13.6	21.7
Methyl isopropenyl ketone	84.1	0.847	14.0	10.3	7.1	18.8
Methyl isopropyl ketone	86.1	0.798	14.6	8.8	6.6	18.3
Methyl methacrylate	100.1	0.930	13.7	9.8	6.1	17.9
1-Methyl-2,5-*endo*methylenecyclohexane-1-methanol	126.2	0.998	14.6	7.5	21.6	27.2
1-Methylnaphthalene	142.2	1.014	17.9	9.5	0.0	20.3
2-Methylnonane	142.3	0.723	15.5	0.0	0.0	15.5
3-Methylnonane	142.3	0.728	15.7	0.0	0.0	15.7
4-Methylnonane	142.3	0.727	15.7	0.0	0.0	15.7
5-Methylnonane	142.3	0.728	15.6	0.0	0.0	15.6
2-Methyloctane	128.3	0.708	15.4	0.0	0.0	15.4
3-Methyloctane	128.3	0.716	15.4	0.0	0.0	15.4
4-Methyloctane	128.3	0.715	15.4	0.0	0.0	15.4
2-Methylpentanal	100.2	0.805	14.1	8.0	7.1	17.7
2-Methylpentane	86.2	0.648	14.4	0.0	0.8	14.4
3-Methylpentane	86.2	0.659	14.6	0.0	0.0	14.6
2-Methyl-1,3-pentanediol	118.2	0.969	13.0	10.9	18.6	25.2
2-Methyl-1,5-pentanediol	118.2	0.970	14.2	11.6	20.6	27.6
2-Methylpentanoic acid	116.2	0.918	15.6	8.9	11.8	21.5
2-Methylpentanol	102.2	0.820	14.2	8.5	12.6	20.8
2-Methyl-2-pentanol	102.2	0.811	13.3	9.2	11.1	19.6
2-Methyl-3-pentanol	102.2	0.820	14.7	8.0	12.1	20.6
3-Methylpentanol	102.2	0.819	14.8	8.6	13.0	21.5
3-Methyl-2-pentanol	102.2	0.825	15.2	8.2	12.6	21.4
3-Methyl-3-pentanol	102.2	0.824	11.4	8.7	10.1	17.5
4-Methylpentanol	102.2	0.809	15.6	8.7	13.4	22.3
2-Methyl-2-pentenal	98.2	0.851	14.8	9.6	7.7	19.2
2-Methyl-1-pentene	84.2	0.674	14.1	3.9	3.2	14.9
2-Methyl-2-pentene	84.2	0.680	14.4	3.8	3.4	15.3
3-Methyl-1-pentene	84.2	0.662	13.7	3.7	2.9	14.5

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
4-Methyl-1-pentene	84.2	0.658	13.6	3.7	3.0	14.4
cis-4-Methyl-2-pentene	84.2	0.664	14.2	3.5	0.0	14.6
trans-4-Methyl-2-pentene	84.2	0.663	14.4	3.3	0.0	14.7
4-Methyl-2-pentyl acetate	144.2	0.853	14.4	7.0	3.0	16.3
4-Methyl-2-pentyl butyrate	172.3	0.849	14.1	6.2	3.6	15.8
2-Methylpentyl Cellosolve®	146.2	0.882	13.6	7.2	11.4	19.2
4-Methyl-2-pentyl Cellosolve	146.2	0.874	13.4	7.3	10.6	18.6
N-Methylpiperazine	100.2	0.898	16.7	9.0	5.2	19.6
2-Methylpropane, isobutane	58.1	0.550	12.5	0.0	0.0	12.5
2-Methylpropene, isobutylene	56.1	0.587	12.6	4.2	3.0	13.6
Methyl 1-propenyl ether	72.1	0.771	14.7	7.3	7.8	18.2
Methyl propionate	88.1	0.909	13.9	8.8	8.9	18.7
Methyl propyl ketone	86.1	0.801	14.6	8.8	7.0	18.4
2-Methyl-2-propylpentanol	144.3	0.838	14.3	7.3	10.2	19.0
N-Methyl-2-pyrrolidone	99.1	1.020	16.5	10.4	13.5	23.7
α-Methylstyrene	118.2	0.905	16.6	8.5	0.0	18.6
2-Methyl-1,2,3,6-tetrahydrobenzaldehyde	124.2	0.942	15.4	9.5	6.5	19.2
4-Methyltetrahydropyran	100.2	0.953	15.8	6.3	0.0	17.0
2-Methylthioethyl acrylate	146.2	1.060	14.4	11.5	7.9	20.1
2-Methylthiophene	98.2	1.012	15.1	12.1	2.6	19.5
3-Methylthiophene	98.2	1.015	15.2	12.1	1.8	19.5
Monoethanolamine, 2-aminoethanol	61.1	1.012	13.9	13.8	25.0	31.8
Monoisopropanolamine, isopropanolamine	75.1	0.956	13.9	12.3	20.1	27.3
Morpholine	87.1	0.995	16.0	11.4	10.1	22.1
Nitrobenzene	123.1	1.190	17.6	14.0	0.0	22.5
Nitroethane	75.1	1.045	19.0	13.0	0.0	23.0
1-Nitropropane	89.1	0.996	18.1	11.2	0.0	21.3
2-Nitropropane	89.1	0.985	16.5	10.4	6.6	20.6
Nonane	128.3	0.713	15.6	0.0	0.0	15.6
1-Nonanol	144.3	0.823	15.3	7.3	12.0	20.7
sec-Nonanol	144.3	0.819	13.9	6.6	10.3	18.5
1-Nonene	126.2	0.724	15.4	3.4	0.0	15.8
Nonylbenzene	204.3	0.851	16.0	6.8	0.0	17.4
Nonyl Cellosolve®	188.3	0.865	13.7	6.4	9.2	17.7
1-Nonylynaphthalene	254.4	0.932	17.4	6.6	0.0	18.6
Nonylphenol	220.4	0.941	15.6	6.7	9.1	19.3
Octane	114.2	0.698	15.4	0.0	0.0	15.4
1-Octanol	130.2	0.822	15.2	7.7	12.4	21.1
2-Octanol	130.2	0.817	14.1	6.9	10.9	19.1
1-Octene	112.2	0.710	15.0	3.5	2.3	15.5
cis-2-Octene	112.2	0.719	15.1	3.2	0.0	15.5
trans-2-Octene	112.2	0.714	15.1	3.0	0.0	15.4
cis-3-Octene	112.2	0.716	15.1	3.2	0.0	15.5
trans-3-Octene	112.2	0.710	15.1	3.0	0.0	15.4
cis-4-Octene	112.2	0.716	15.1	3.2	0.0	15.4
trans-4-Octene	112.2	0.709	15.1	3.0	0.0	15.4
Octylbenzene	190.3	0.851	16.7	5.4	0.0	17.5
1,4-Oxathiane	104.2	1.112	16.8	12.3	5.2	21.5
Pentadecane	212.4	0.764	16.8	0.0	0.0	16.8
trans-1,3-Pentadiene	68.1	0.671	14.1	5.3	4.8	15.8
Pentane	72.2	0.621	14.4	0.0	0.0	14.4
1,5-Pentanediol	104.2	0.987	13.9	12.2	22.8	29.4
1-Pentanol, amyl alcohol	88.2	0.811	14.8	9.1	14.7	22.7
2-Pentanol, *sec*-amyl alcohol	88.2	0.805	15.0	8.5	13.7	22.0

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
3-Pentanol	88.2	0.816	13.9	8.3	13.0	20.8
1-Pentene	70.1	0.635	13.9	4.1	0.0	14.5
cis-2-Pentene	70.1	0.649	14.5	3.8	0.0	15.0
trans-2-Pentene	70.1	0.642	14.1	3.4	3.6	14.9
Pentyl acetate	130.2	0.869	14.3	7.3	5.7	17.1
Pentylcyclohexane	154.3	0.799	16.0	2.3	0.0	16.1
Perchloroethylene, tetrachloroethylene	165.9	1.611	11.4	15.2	0.0	19.0
Phenoxypropylene oxide	150.2	1.104	17.6	11.8	7.6	22.5
Phenyl Carbitol®	182.2	1.109	14.4	10.4	14.3	22.9
Phenyl Cellosolve®	138.2	1.103	13.7	10.4	16.0	23.5
Phenyl Cellosolve® acetate	180.2	1.101	16.2	11.1	8.8	21.5
N-Phenylethanolamine	137.2	1.091	15.2	11.9	17.0	25.7
Phenylhydrazine	108.1	1.095	15.6	14.9	13.7	25.5
N-Phenylpiperazine	162.2	1.064	18.1	11.4	3.2	21.6
Picoline	93.1	0.950	18.2	7.8	6.8	20.9
Pinacolyl alcohol	102.2	0.815	14.2	8.0	10.6	19.5
α-Pinene	136.2	0.853	15.6	4.3	0.0	16.2
Piperidine	85.2	0.857	16.2	8.7	5.8	19.3
Pivaldehyde	86.1	0.786	13.4	8.5	5.5	16.8
Polyglycolamine H221M	221.3	1.004	13.9	9.2	10.8	19.8
Propanal, propionaldehyde	58.1	0.791	12.6	9.7	11.0	19.3
Propane	44.1	0.492	11.8	0.0	0.0	11.8
1,3-Propanediol, trimethylene glycol	76.1	1.050	12.4	14.1	27.1	33.0
1-Propanol	60.1	0.799	14.1	10.5	17.7	24.9
2-Propanol, isopropanol	60.1	0.781	14.0	9.8	16.0	23.4
Propasol® Solvent B, butoxypropanol	132.2	0.878	13.2	7.5	11.5	19.0
Propasol® Solvent DM	148.2	0.955	13.1	8.6	12.2	19.8
Propasol® Solvent M	90.1	0.917	12.9	9.2	14.2	21.3
Propasol® Solvent P, propoxypropanol	118.2	0.880	13.2	8.0	12.1	19.5
Propionic acid	74.1	0.988	15.3	11.2	17.1	25.5
Propionic anhydride	130.1	1.005	12.6	11.4	10.4	19.9
Propionitrile	55.1	0.777	12.6	11.5	13.8	22.0
Propyl acetate	102.1	0.881	14.1	8.1	7.8	18.0
Propylamine	59.1	0.712	13.9	9.3	7.2	18.2
Propylbenzene	120.2	0.856	16.2	6.9	0.0	17.6
Propyl Carbitol®	148.2	0.963	13.1	8.4	13.2	20.4
Propyl chloride, see chloropropane						
Propylcyclohexane	126.2	0.788	16.0	2.5	0.0	16.2
Propylcyclopentane	112.2	0.771	16.0	3.1	0.0	16.3
Propylene chlorohydrin	94.5	1.106	12.9	11.6	16.0	23.6
Propylene diamine	74.1	0.858	13.5	12.8	12.8	22.6
Propylene dichloride, see 1,3-dichloropropane						
Propylene glycol, 1,2-propanediol	76.1	1.033	11.8	13.3	25.0	30.7
Propylene oxide, methyloxirane	58.1	0.823	13.6	8.2	10.4	18.9
4-Propylheptane	142.3	0.731	15.3	0.0	0.0	15.3
2-Propylheptanol	158.3	0.828	14.5	6.9	10.6	19.2
m-Propyltoluene	134.2	0.855	16.5	6.3	0.0	17.7
o-Propyltoluene	134.2	0.869	16.7	6.5	0.0	17.9
p-Propyltoluene	134.2	0.853	16.5	6.2	0.0	17.6
Pyridine	79.1	0.978	17.6	10.1	7.7	21.7
Styrene, ethenylbenzene	104.2	0.901	16.8	9.1	0.0	19.1
Styrene oxide, phenyloxirane	120.2	1.048	17.5	11.4	5.1	21.5
α-Terpineol	154.2	0.927	13.9	7.9	10.2	19.0

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
Tetradecane	198.4	0.758	16.6	0.0	0.0	16.6
1,1,3,3-Tetraethoxypropane	220.3	0.913	13.5	7.4	6.7	16.8
1,2,3,6-Tetrahydrobenzaldehyde	110.2	0.966	15.6	10.3	7.6	20.1
1,2,3,6-Tetrahydrobenzoic acid	126.2	1.077	18.6	11.3	13.7	25.7
1,2,3,6-Tetrahydrobenzonitrile	107.2	0.951	15.4	11.5	10.0	21.7
Tetrahydrofuran	72.1	0.882	13.3	11.0	6.7	18.5
1,2,3,4-Tetrahydronaphthalene	132.2	0.964	17.8	7.8	0.0	19.4
Tetrahydropyran-2-methanol	116.2	1.021	14.4	9.6	13.5	22.0
1,1,3,5-Tetramethoxyhexane	206.3	0.952	13.7	7.7	7.1	17.3
2,2,3,3-Tetramethylbutane	114.2	0.820	17.1	0.0	0.0	17.1
N,N,N,N-Tetramethyl-1,3-butanediamine	144.3	0.797	15.2	4.7	2.0	16.0
N,N,N,N-Tetramethyl-1,2-ethylenediamine	116.2	0.772	15.0	5.1	2.7	16.0
2,2,3,3-Tetramethylpentane	128.3	0.746	15.2	0.0	0.0	15.2
N,N,N,N-Tetramethyl-1,3-propanediamine	130.2	0.777	15.1	4.8	2.6	16.1
2-Thiabutane	76.2	0.835	14.6	8.7	5.7	17.9
Thiacyclopentane, tetrahydrothiophene	88.2	0.992	17.4	10.9	0.6	20.5
2-Thiapropane	62.1	0.841	14.2	9.6	6.7	18.4
Thiophene	84.1	1.057	14.0	12.4	7.5	20.0
Toluene, methylbenzene	92.1	0.862	16.4	8.0	1.6	18.3
Tolylene diisocyanate	174.2	1.212	15.3	16.4	7.8	23.7
N-(*o*-Tolyl)ethanolamine	151.2	1.067	14.3	10.9	15.0	23.4
Triallylamine	137.2	0.795	13.8	6.6	4.1	15.8
Tributylamine	185.4	0.775	15.1	2.8	4.0	15.9
1,1,1-Trichloroethane, methyl chloroform	133.4	1.218	10.8	11.5	0.0	15.8
1,1,2-Trichloroethane	133.4	1.432	13.9	12.9	7.0	20.2
1,1,2-Trichloroethylene	131.4	1.455	11.7	14.0	4.4	18.7
Trichloromethane	119.4	1.477	11.0	13.7	6.3	18.7
1,2,3-Trichloropropane	147.4	1.384	14.8	12.7	6.7	20.6
2,2,3-Trichloropropionaldehyde	161.4	1.467	11.0	14.6	8.0	20.0
Tridecane	184.4	0.751	16.4	0.0	0.0	16.4
1,1,3-Triethoxy-4-ethyloctane	275.5	0.866	14.0	5.6	4.8	15.9
Triethylamine	101.2	0.723	14.6	3.7	1.9	15.2
Triethylene glycol	150.2	1.249	15.0	12.2	21.8	29.1
Triethylenetetramine	146.2	0.976	12.7	12.4	14.1	22.8
Triglycol dichloride	187.0	1.190	15.3	10.5	9.6	20.9
1,1,3-Trimethoxybutane	148.2	0.916	13.6	7.8	6.6	17.0
1,2,3-Trimethylbenzene	120.2	0.889	17.3	7.3	0.0	18.7
1,2,4-Trimethylbenzene	120.2	0.870	16.9	7.1	0.0	18.3
1,3,5-Trimethylbenzene, mesitylene	120.2	0.860	16.7	7.0	0.0	18.1
2,2,3-Trimethylbutane	100.2	0.685	14.2	0.0	0.0	14.2
1,1,2-Trimethylcyclopentane	112.2	0.767	15.1	3.0	0.0	15.4
1,1,3-Trimethylcyclopentane	112.2	0.742	14.6	2.9	0.0	14.9
2,2,3-Trimethylheptane	142.3	0.737	15.2	0.0	0.0	15.2
2,2,4-Trimethylheptane	142.3	0.722	14.6	0.0	0.0	14.6
2,2,5-Trimethylheptane	142.3	0.721	14.7	0.0	0.0	14.7
2,2,6-Trimethylheptane	142.3	0.714	14.6	0.0	0.0	14.6
2,3,3-Trimethylheptane	142.3	0.743	15.3	0.0	0.0	15.3
2,3,4-Trimethylheptane	142.3	0.746	15.4	0.0	0.0	15.4
2,3,5-Trimethylheptane	142.3	0.736	15.0	0.0	0.0	15.0
2,3,6-Trimethylheptane	142.3	0.729	14.9	0.0	0.0	14.9
2,4,4-Trimethylheptane	142.3	0.728	14.8	0.0	0.0	14.8
2,4,5-Trimethylheptane	142.3	0.736	15.0	0.0	0.0	15.0
2,4,6-Trimethylheptane	142.3	0.717	14.5	0.0	0.0	14.5
2,5,5-Trimethylheptane	142.3	0.731	14.8	0.0	0.0	14.8

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
3,3,4-Trimethylheptane	142.3	0.752	15.4	0.0	0.0	15.4
3,3,5-Trimethylheptane	142.3	0.737	15.0	0.0	0.0	15.0
3,4,4-Trimethylheptane	142.3	0.752	15.4	0.0	0.0	15.4
3,4,5-Trimethylheptane	142.3	0.754	15.4	0.0	0.0	15.4
2,2,3-Trimethylhexane	128.3	0.724	15.0	0.0	0.0	15.0
2,2,4-Trimethylhexane	128.3	0.710	14.5	0.0	0.0	14.5
2,2,5-Trimethylhexane	128.3	0.702	14.5	0.0	0.0	14.5
2,3,3-Trimethylhexane	128.3	0.733	15.1	0.0	0.0	15.1
2,3,4-Trimethylhexane	128.3	0.734	15.2	0.0	0.0	15.2
2,3,5-Trimethylhexane	128.3	0.717	14.8	0.0	0.0	14.8
2,4,4-Trimethylhexane	128.3	0.719	14.7	0.0	0.0	14.7
3,3,4-Trimethylhexane	128.3	0.740	15.3	0.0	0.0	15.3
2,6,8-Trimethyl-4-nonanol	186.3	0.814	13.9	5.9	7.8	16.9
2,2,3-Trimethylpentane	114.2	0.711	14.7	0.0	0.0	14.7
2,2,4-Trimethylpentane, isooctane	114.2	0.687	14.0	0.0	0.0	14.0
2,3,3-Trimethylpentane	114.2	0.721	14.8	0.0	0.0	14.8
2,3,4-Trimethylpentane	114.2	0.714	14.9	0.0	0.0	14.9
2,2,4-Trimethylpentanol	130.2	0.825	14.3	7.7	9.9	19.0
2,2,4-Trimethyl-3-pentenyl acetate	170.3	0.892	15.2	7.6	0.0	17.0
2,2,4-Trimethylpentyl acetate	172.3	0.861	14.8	6.5	1.1	16.2
2,4,6-Trimethyl-1,2,3,6-tetrahydrobenzaldehyde	152.2	0.914	14.7	8.2	5.3	17.7
Undecane	156.3	0.735	16.0	0.0	0.0	16.0
1-Undecanol	172.3	0.828	15.4	6.7	11.2	20.2
2-Undecanol	172.3	0.823	13.9	6.0	9.8	18.0
Valeraldehyde, 1-pentanal	86.1	0.805	13.8	8.4	8.8	18.4
Valeric acid	102.1	0.934	16.7	9.7	14.3	24.0
Vinyl acetate	86.1	0.926	12.9	10.0	8.7	18.5
Vinyl allyl ether	84.1	0.798	13.2	7.9	7.0	16.8
Vinyl butyl Carbitol®	188.3	0.913	14.2	7.3	8.0	17.9
Vinyl butyl ether	100.2	0.774	13.8	6.1	5.5	16.1
Vinyl *S*-butylmercaptoethyl ether	160.3	0.921	15.0	8.5	5.9	18.2
Vinyl butyrate	114.2	0.895	13.8	8.7	7.0	17.7
Vinyl Carbitol®	132.2	1.023	13.3	9.9	15.3	22.6
Vinyl 2-chloroethyl ether	106.6	1.041	14.2	9.9	8.7	19.4
Vinyl crotonate	112.1	0.937	14.0	10.0	8.4	19.2
Vinyl ethyl Carbitol®	160.2	0.932	14.0	8.0	8.6	18.3
Vinyl ethyl ether	72.1	0.748	13.2	7.0	5.7	16.0
Vinyl 2-ethylhexanoate	170.3	0.869	14.0	7.0	5.2	16.6
Vinyl 2-ethylhexyl ether	156.3	0.805	14.9	5.2	4.5	16.3
Vinyl *S*-ethylmercaptoethyl ether	132.2	0.946	14.9	9.6	6.6	18.9
Vinyl isobutyl ether	100.2	0.763	14.4	6.3	4.0	16.2
Vinyl isopropyl ether	86.1	0.747	13.6	6.6	4.2	15.7
Vinyl methyl Cellosolve®	102.1	0.890	14.0	8.4	8.6	18.4
Vinyl methyl ether	58.1	0.742	10.5	7.0	6.8	14.4
Vinyl propionate	100.1	0.910	13.5	9.4	7.7	18.1
Vinyl propyl ether	86.1	0.762	13.5	6.5	5.9	16.1
m-Vinyltoluene	118.2	0.905	16.8	8.3	0.0	18.7
o-Vinyltoluene	118.2	0.897	16.8	8.4	0.0	18.8
p-Vinyltoluene	118.2	0.904	16.9	8.2	0.0	18.8
Vinyl 2,6,8-trimethyl-4-nonyl ether	212.4	0.802	14.5	4.4	1.5	15.3
Water	18.02	0.997	12.2	22.8	40.4	48.0

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
m-Xylene, 1,3-dimethylbenzene	106.2	0.860	16.5	7.2	2.4	18.2
o-Xylene, 1,2-dimethylbenzene	106.2	0.876	17.0	7.5	0.0	18.5
p-Xylene, 1,4-dimethylbenzene	106.2	0.856	16.5	7.0	2.0	18.1

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

5.12 OTHER MULTICOMPONENT COHESION PARAMETERS

Beerbower, Martin, and Wu[31,32] developed a four-component approach to the solubilities of solids in polar and nonpolar systems which is intermediate in complexity between five-component parameters and the three-component Hansen method. Induction parameters were ignored on the grounds that they did not improve significantly the solubility predictions, so Equation 24 reduces to

$$\delta_t^2 = \delta_d^2 + \delta_o^2 + 2\,\delta_a\delta_b \tag{75}$$

If δ_o is identified with δ_p and $\delta_h^2 = 2\,\delta_a\,\delta_b$, the three-component Hansen parameters are recovered. But, more importantly, Equation 21 simplifies to

$$^{ij}A = ({}^i\delta_d - {}^j\delta_d)^2 + ({}^i\delta_p - {}^j\delta_p)^2 + 2({}^i\delta_a - {}^j\delta_a)({}^i\delta_b - {}^i\delta_b) \tag{76}$$

The value of δ_b can be determined[143] from the spectroscopic proton-accepting parameter β, and δ_a can then be calculated from $(\delta_t^2 - \delta_d^2 - \delta_p^2/2\delta_b)$. The original data set by this method appears in Table 21. The δ_p and δ_d values were based on those of Hansen and Beerbower[25] (Table 11) with a few corrections, and some of the component parameters were adjusted on the basis of solubility observations. If a larger set of data is developed, this four-parameter method may become a generally acceptable improvement on the Hansen method, as it takes into account the unsymmetrical nature of hydrogen-bonding interactions.

The Hansen component parameters have been combined in various alternative ways. Sometimes δ_p and δ_h (the "association" interactions) are described collectively:

$$\delta_{hp}^2 = \delta_h^2 + \delta_p^2 = \delta_t^2 - \delta_d^2 \tag{77}$$

Beerbower and Jensen[35] developed a semiquantitative approach to the prediction of the hard/soft character of Lewis acid-base species using a sorting map based on the composite association parameter δ_{hp} and the dispersion parameter. On this map, alkanes, aromatics and sulfides were soft, oxygen donor species were hard, and anilines and pyridines were borderline. The ratio δ_{hp}/δ_d was critical, reflected in a softness value (based on a zero value for water) defined as

$$S = 20.1 - (\delta_{hp}/\text{MPa}^{1/2})/((\delta_d/\text{MPa}^{1/2}) - 13.3) \tag{78}$$

Table 22 lists Lewis base liquids according to the hard/borderline/soft classification, together with softness values defined as in Equation 78. Lewis acids such as glycols and carboxylic acids appeared in the hard region; trichloromethane was in the soft region.

TABLE 19
Three-Component Cohesion Parameters for Alkyl Derivatives of Phenol and Resorcinol From Vaporization, Distribution Coefficient, and Gas Chromatographic Data

	20°C		80°C			
	δ/MPa$^{1/2}$ (vaporization data)	δ/MPa$^{1/2}$ (distribution data)	δ_t/MPa$^{1/2}$	δ_d/MPa$^{1/2}$	δ_p/MPa$^{1/2}$	δ_h/MPa$^{1/2}$
			Alkylphenols, Ph(OH)R			
—	24.6	25.8	23.1	17.8	5.5	13.9
2-C_1	22.7	23.1	21.5	17.2	0.8	12.9
2-C_2	21.9	—	20.7	16.4	3.3	11.9
2-C_3	21.3	—	19.8	16.0	3.7	11.3
2-C_4	20.9	—	19.2	15.6	4.3	10.4
2-C_5	20.3	—	18.6	14.9	4.9	10.0
2-C_6	19.8	—	18.2	14.5	5.5	9.4
3- and 4-C_1	23.9	25.0	22.3	17.0	6.8	12.9
3- and 4-C_2	23.3	22.1	21.7	16.6	7.2	11.9
3- and 4-C_3	22.9	—	21.1	16.0	7.6	11.3
3- and 4-C_4	22.3	—	20.5	15.6	8.0	10.4
3- and 4-C_5	21.9	—	20.1	15.3	8.2	10.0
3- and 4-C_6	21.5	—	19.4	14.7	8.6	9.4
2,6-$(C_1)_2$	21.9	—	20.7	16.6	2.9	11.9
2,4-$(C_1)_2$	22.5	22.9	20.7	16.6	2.9	11.9
2,3-$(C_1)_2$	22.3	22.9	20.7	16.6	2.9	11.9
3,5-$(C_1)_2$	23.7	23.1	21.7	16.6	7.2	11.9
3,4-$(C_1)_2$	23.1	23.1	21.7	16.6	7.0	11.9
			Alkylresorcinols, Ph-1,3-$(OH)_2$R			
—	31.5	30.1	29.5	18.4	11.3	20.1
2-C_1	27.8	28.2	26.0	17.6	5.7	18.2
2-C_2	27.2	27.6	25.2	17.0	7.8	17.0
2-C_3	26.6	27.0	24.3	16.6	8.2	15.8
2-C_4	26.2	26.6	23.9	16.2	9.4	14.9
2-C_5	25.8	26.4	23.3	15.6	10.0	14.1
2-C_6	25.6	26.2	22.9	15.1	10.6	13.5
2-C_7	25.4	25.8	22.7	14.7	11.5	13.1
2-C_8	25.0	—	22.5	14.3	12.1	12.5
4-C_1	28.4	28.6	26.4	17.6	7.4	18.2
4-C_2	27.6	27.8	25.6	17.2	8.6	17.0
4-C_3	27.0	27.2	25.0	16.6	9.8	15.8
4-C_4	26.6	26.6	24.3	16.4	10.0	14.9
4-C_5	26.2	26.2	23.9	16.0	10.8	14.1
4-C_6	25.8	25.8	23.7	15.3	12.1	13.5
4-C_7	25.6	25.6	23.3	14.9	12.3	13.1
4-C_8	25.4	—	23.1	14.5	12.9	12.5
5-C_1	30.1	29.1	27.8	18.0	10.8	18.2
5-C_2	29.1	28.2	27.0	17.4	11.9	17.0
5-C_3	28.4	27.6	26.2	17.0	12.1	15.8
5-C_4	27.8	27.0	25.6	16.6	12.5	14.9
5-C_5	27.4	26.8	25.0	16.2	12.7	14.1
5-C_6	27.0	26.4	24.6	15.8	13.1	13.5
5-C_7	27.0	26.2	24.1	15.3	13.3	13.1
5-C_8	26.4	—	23.9	14.9	13.9	12.5

Adapted from Lille, Ü, Kundle, H., and Eisen, O., *J. Chromatogr.*, 116, 1, 1976.

TABLE 20
Calculated Hansen and Hildebrand Parameters

Liquid	$\delta/\mathrm{MPa}^{1/2}$					
	δ_d	δ_p	δ_h	δ_t[a]	δ_t[b]	δ_t[c]
Hexane	14.9	0.0	0.0	14.9	14.7	14.7
Isohexane	15.0	0.0	0.0	15.0	14.3	14.3
Heptane	15.3	0.0	0.0	15.3	15.0	15.1
Octane	15.5	0.0	0.0	15.5	15.1	15.3
Decane	15.9	0.0	0.0	15.9	15.2	15.2
Dodecane	16.0	0.1	0.0	16.0	15.1	15.6
Cyclohexane	16.2	0.2	0.0	16.2	16.7	17.2
Benzene	17.7	0.3	2.2	17.8	18.5	18.9
Toluene	17.6	0.7	1.8	17.7	18.1	18.2
o-Xylene	17.8	1.0	1.6	17.9	18.2	18.3
Phenol	18.5	5.3	16.2	25.1	22.8	—
Ethylbenzene	17.6	0.8	1.6	17.7	17.8	17.2
Methylcyclohexane	16.1	0.1	0.0	16.1	16.2	—
Acetone	14.7	11.5	5.6	19.5	19.1	—
Methanol	18.6	0.5	1.9	18.7	18.7	—
Nefras S-155/200 (mineral spirits)	16.3	1.0	0.6	16.3	16.3	15.8
Nefras S-80/120 (BR-2)	15.4	0.4	0.2	15.4	14.9	14.9
Nefras AR-120/200	17.8	0.5	1.7	17.9	17.4	17.6

[a] $\delta_d^2 + \delta_p^2 + \delta_h^2$

[b] From vaporization enthalpy.

[c] From surface tension, $\delta_t/\mathrm{MPa}^{1/2} = 4.1\,(\gamma/{}^{l}V^{1/3})^{0.43}$

Adapted from Stekol'shchikov, M. N., Krivtsova, L. M., and Ratner, M. I., *Khim. Tekhnol. Topl. Masel*, (6), 33, 1987; *Chem. Technol. Fuels Oils*, (6), 292, 1987.

An alternative combination of component cohesion parameters[144,145] uses a cohesion parameter determined from gas-liquid chromatography (Chapter 18) and given by $(\Delta H_{add}/V)^{1/2}$ where ΔH_{add} is the "additional" enthalpy of solution (the enthalpy of solution less the contributions from dispersion and induced dipole interactions).

Wingefors[146,147] extended the polar-nonpolar approach (Section 5.8) for solvent extraction in terms of a proton donor parameter, δ_σ:

$$\delta_t^2 = \delta_\lambda^2 + \delta_\tau^2 + k\delta_\lambda\,\delta_\tau + \delta_\sigma\delta_\tau \tag{79}$$

The terms on the right-hand side represent dispersion, dipole-dipole, dipole-induced dipole, and hydrogen-bonding components, respectively; the combination of the dipole parameter δ_τ with the proton donor parameter δ_σ follows from the assumption that proton acceptor ability and electron donor ability should be correlated in some way. Comparison with other equations suggests:

$$\delta_\lambda^2 \approx \delta_d^2 \tag{80}$$

$$\delta_\tau^2 + k\delta_\lambda\delta_\tau \approx \delta_p^2 \approx 2\delta_i\delta_d \tag{81}$$

$$\delta_\sigma\,\delta_\tau \approx 2\delta_a\delta_b \tag{82}$$

Bagley, Nelson, and Scigliano[148] suggested that their cohesion parameters δ_V and δ_R (based on internal pressure considerations as indicated in Section 7.5) are related to Hansen parameters:

TABLE 21
Four-Component Cohesion Parameters for Common Liquids

	δ/MPa$^{1/2}$						
Liquid	δ_d	δ_p	δ_a	δ_b	δ_h	δ_t	${}^{l}V$ cm^3 mol^{-1}
Pentane	14.5	0.0	0.0	0.0	0.0	14.5	116
Hexane	14.9	0.0	0.0	0.0	0.0	14.9	132
Heptane	15.3	0.0	0.0	0.0	0.0	15.3	148
Nonane	15.8	0.0	0.0	0.0	0.0	15.8	180
Decane	15.8	0.0	0.0	0.0	0.0	15.8	196
Cyclohexane	16.8	0.0	0.0	0.0	0.0	16.8	109
Benzene	18.4	1.0	1.4	1.4	2.0	18.6	89
Toluene	18.0	1.4	1.6	1.2	2.0	18.2	107
Chlorobenzene	19.0	4.3	2.0	1.0	2.0	19.6	102
1,2-Dichloroethane	19.0	7.4	4.1	2.0	4.1	20.8	79
1,1-Dichloroethane	16.6	8.2	0.4	0.2	0.4	18.5	85
Trichloromethane	17.8	3.1	6.1	2.7	5.7	18.9	81
Tetrachloromethane	17.8	0.0	0.1	1.8	0.6	17.8	97
1,2-Dibromoethane	19.0^{a}	3.5	22.9	1.6	8.6	21.2	87
1,1-Dibromoethane	18.4^{a}	5.1^{a}	20.5	1.0	19.6^{a}	20.2	93
Diethyl ether	14.5	2.9	1.0	12.9	5.1	15.7	105
Dipropyl ether	14.9	2.3	0.8	10.2	4.1	15.6	139
Dibutyl ether	15.6	1.6	0.6	8.0	3.1	15.9	170
Ethyl acetate	15.1	5.3	10.8	3.9	9.2	18.5	99
Propyl acetate	15.8	4.3	6.8	7.4	3.1	17.7	116
Butyl acetate	15.8	3.9	6.3	5.7	3.5	17.4	133
Hexyl acetate	16.0	3.1	5.9	3.9	4.5	17.3	165
Carbon disulfide	20.5	0.0	0.4	0.4	0.6	20.5	60
Acetone	15.5	10.4	4.9	4.9	7.0	20.0	74
1,4-Dioxane	19.0	1.8	2.1	13.3	7.4	20.5	86
Aniline	19.4	5.1	3.9	13.3	10.2	22.5	92
Nitrobenzene	20.1	8.6	4.1	2.1	4.1	22.2	103
Acetophenone	19.6	8.6	2.3	3.1	3.7	21.7	117
Benzyl alcohol	18.4	6.3	12.1	7.8	13.7	23.8	104
Cyclohexanol	17.4	4.1	14.9	6.1	13.5	22.4	106
Methanol	15.1	12.3	17.2	22.3	22.3	29.6	41
Ethanol	15.8	8.8	17.0	11.3	19.4	26.5	59
1-Propanol	16.0	6.8	15.3	9.8	17.4	24.5	75
2-Propanol	15.8	6.1	14.5	9.2	16.4	23.5	77
1-Butanol	16.0	5.7	13.1	9.4	15.8	23.1	92
Isobutanol	15.1	5.7	12.3	10.4	16.0	22.8	92
2-Butanol	15.8	5.7	13.5	7.8	14.5	22.2	93
tert-Butanol	14.9	5.1	19.6	4.9	13.9	21.0	94
1-Pentanol	16.0	4.5	11.1	8.8	13.9	21.7	109
1-Hexanol	16.4	4.3	11.1	7.2	12.9	21.3	125
1-Heptanol	16.6	4.1	10.8	7.0	12.3	21.0	142
1-Octanol	17.0	3.3	10.6	6.6	11.9	20.9	158
Ethylene glycol	17.0	11.1	36.6	9.0	25.8	32.7	56
1,2-Propanediol	16.8	9.4	28.8	9.4	23.3	30.2	74
1,3-Propanediol	16.6	10.8	22.3	15.1	26.0	32.7	73
Glycerol	17.4	12.1	40.1	10.4	29.3	36.1	73
1,4-Butanediol	16.8	16.6	37.2	7.6	23.7	33.5	89
Acetic acid	14.5	8.0	14.3	6.3	13.5	21.4	58
Propionic acid	14.7	7.8	12.3	6.1	12.3	20.7	75
Butyric acid	14.9	4.1	13.1	4.3	10.6	18.8	92
Dimethylsulfoxide	18.4	16.4	4.5	11.7	10.2	26.7	71
Pyridine	19.0	8.8	2.9	6.6	6.1	21.8	81
Formamide	17.2	26.2	11.7	15.6	19.0	36.7	40
N-Methylformamide	17.2	20.7	9.8	8.0	12.5	29.6	59

TABLE 21 (continued)
Four-Component Cohesion Parameters for Common Liquids

Liquid	δ_d	δ_p	δ_a	δ_b	δ_h	δ_t	${}^iV$ cm^3 mol^{-1}
	δ/MPa$^{1/2}$						
N,N-Dimethylformamide	17.4	13.7	7.0	9.0	11.3	24.8	77
N,N-Diethylformamide	16.8	11.5	5.5	7.0	8.8	22.1	112
N,N-Dimethylacetamide	16.8	11.5	5.9	8.8	10.2	22.7	93
N,N-Diethylacetamide	16.8	8.4	4.3	6.6	7.6	20.2	127
Water	15.6	16.0	13.7	65.5	42.3	47.9	18

[a] Recalculated by Beerbower et al.

Adapted from Beerbower, A., Wu, P. L., and Martin, A., *J. Pharm. Sci.*, 73, 179, 1984.

$$\delta_V^2 \approx \delta_d^2 + \delta_p^2 \approx \delta_d^2 + \delta_o^2 + 2\delta_i\delta_d \tag{83}$$

and

$$\delta_R^2 \approx \delta_h^2 \approx 2\delta_a\delta_b \tag{84}$$

As shown above (Section 5.6), Munafo, Buchmann, Hô Nam-Tran and Kesselring[37] used $\delta_h^2 = 2\,\delta_a\,\delta_b$ for δ_h which they evaluated instead of δ_a and δ_b, together with δ_d, δ_i, δ_o, and $\delta_p = (\delta_o^2 + 2\,\delta_i\,\delta_d)^{1/2}$.

Obviously there are many such ways of subdividing the Hildebrand or total cohesion parameter to provide component or composite parameters that are simpler to use than the full set of five parameters, but less general. The choice finally made in each case depends on the particular application.

It is important to remember that cohesion parameter values are derived from many different types of information, both theoretical and experimental, and they will not all be in good agreement with each other. The aim should be to select a cohesion parameter method that is appropriate for the particular task, and to determine the values for all the necessary materials. The greater the extent of polar and specific interactions that occur in the systems investigated, the greater the divergence between different methods is likely to be. Other solubility scales are outlined in Chapter 8.

5.13 MODIFIED SEPARATION OF COHESIVE ENERGY DENSITY

Thomas and Eckert[149] proposed a *mo*dified *s*eparation of *c*ohesive *e*nergy *d*ensity (MOSCED) model to predict limiting activity coefficients (Section 7.8) using only pure component parameters. They achieved an average error of only 9% for over 3000 limiting activity coefficients in aprotic and protic (but non-aqueous) systems over wide temperature ranges, with very few errors greater than 30%.

They first considered an equation of the form

$$\begin{aligned} {}^{ij}A = {} & ({}^i\delta_\chi - {}^j\delta_\chi)^2 + ({}^i\delta_\tau - {}^j\delta_\tau)^2 + \\ & ({}^i\delta_\psi - {}^j\delta_\psi)({}^i\delta_\tau - {}^j\delta_\tau) + ({}^i\delta_\alpha - {}^j\delta_\alpha)({}^i\delta_\beta - {}^j\delta_\beta) \end{aligned} \tag{85}$$

TABLE 22
Softness of Lewis-Base Liquids Determined From Hansen Parameters

Liquid	Classification	S
Saturated Hydrocarbons		
Pentane	Soft	20.1
Hexane	Soft	20.1
Heptane	Soft	20.1
Decane	Soft	20.1
Cyclohexane	Soft	20.1
Aromatic Hydrocarbons		
Ethylbenzene	Soft	19.8
o-Xylene, 1,2-dimethylbenzene	Soft	19.4
Toluene, methylbenzene	Soft	19.6
Benzene	Soft	19.7
Naphthalene	Soft	19.3
Sulfides		
Diethyl sulfide	Soft	19.0
Dimethyl sulfide	Soft	18.7
Carbon disulfide	Soft	19.1
Anilines		
Aniline	Borderline	18.2
o-Toluidine, 2-methylaniline	Borderline	18.4
Pyridines		
2,4,6-Trimethylpyridine	Borderline	18.4
2,6-Dimethylpyridine	Borderline	18.3
4-Methylpyridine, γ-picoline	Borderline	18.2
Pyridine	Borderline	18.2
Ethers		
Diethyl ether	Hard	15.3
Dipropyl ether	Hard	17.2
Anisole, methyl phenyl ether	Borderline	18.3
Ketones		
Acetone, 2-propanone	Hard	14.6
3-Pentanone, diethyl ketone	Hard	16.2
2-Butanone, methyl ethyl ketone	Hard	15.4
Cyclohexanone	Hard	17.9
Acetophenone, phenyl methyl ketone	Borderline	18.6
Esters		
Ethyl acetate	Hard	14.7
Propyl acetate	Hard	16.9
Butyl acetate	Hard	17.1
Hexyl acetate	Hard	17.6

TABLE 22 (continued)
Softness of Lewis-Base Liquids Determined From Hansen Parameters

Liquid	Classification	S
Aliphatic Amines		
Butylamine	Hard	17.0
Propylamine	Hard	17.4
Nitriles		
Acetonitrile	Hard	10.8
Propionitrile	Hard	12.8
Butyronitrile	Hard	13.5
Benzonitrile	Hard	17.8
Nitro Compounds		
Nitromethane	Hard	12.1
Nitroethane	Hard	14.1
2-Nitropropane	Hard	15.1
Nitrobenzene	Borderline	18.7
Water		
Water	Hard	0.0
Alcohols		
Methanol	Hard	6.2
Isobutanol, 2-methyl-1-propanol	Hard	10.9
tert-Butanol, 2-methyl-2-propanol	Hard	11.1
Ethanol	Hard	11.4
2-Propanol	Hard	13.0
2-Butanol	Hard	13.8
1-Propanol	Hard	13.1
1-Butanol	Hard	13.8
1-Hexanol	Hard	15.6
1-Octanol	Hard	16.8
Cyclohexanol	Hard	16.4
Benzyl alcohol	Hard	17.1
Amides		
N-Diethylacetamide	Hard	16.9
N,N-Dimethylacetamide	Hard	15.7
N,N-Diethylformamide	Hard	15.9
N-Methylformamide	Hard	13.9
Formamide	Hard	11.8
N,N-Dimethylformamide	Hard	15.8
Sulfoxide		
Dimethylsulfoxide	Hard	11.8

Adapted from Beerbower, A. and Jensen, W. B., *Inorg. Chim. Acta*, 75, 193, 1983.

where δ_λ is a measure of polarizability; δ_τ is a measure of polarity; δ_ψ reflects the induction interactions; δ_α is the acidity parameter; and δ_β is the basicity parameter. The Hildebrand parameter or total cohesion parameter of component *i* is then

$$ {}^{i}\delta^2 = {}^{i}\delta_\lambda{}^2 + {}^{i}\delta_\tau{}^2 + {}^{i}\delta_\psi {}^{i}\delta_\tau + {}^{i}\delta_\alpha {}^{i}\delta_\beta \tag{86} $$

(This is similar to the formulation of Karger, Snyder, et al., but does not include the factors of 2 associated with the induction and acid-base cross-terms in Equations 21 and 23.) Equation 85 was simplified into a form analogous to that of Weimer and Prausnitz (Section 5.8),

$$ \begin{aligned} {}^{ij}A = ({}^{i}\delta_\lambda - {}^{j}\delta_\lambda)^2 &+ {}^{i}q^2 {}^{j}q^2 ({}^{i}\delta_\tau - {}^{j}\delta_\tau)^2 \\ &+ ({}^{i}\delta_\alpha - {}^{j}\delta_\alpha)({}^{i}\delta_\beta - {}^{j}\delta_\beta) \end{aligned} \tag{87} $$

where the induction parameter was considered solely a function of degree of unsaturation, with $q = 1.0$ for saturated molecules, 0.9 for aromatics, and values between these limits for unsaturated aliphatics. Two factors, ${}^{i}\psi$ and ${}^{i}\xi$ were included to account for the "asymmetry" in volume fraction dependence due to polarity and hydrogen bonding, respectively. Neglecting the combinatorial term, the ratio of limiting activity coefficients of components *i* and *j* according to Equation 85 are

$$ (\ln {}^{i}f_x^\infty)/(\ln {}^{j}f_x^\infty) = {}^{i}V / {}^{j}V $$

but this was found not to hold in solutions containing polar molecules. For example, pure ethanol is strongly hydrogen-bonded, but at infinite dilution in cyclohexane, ethanol molecules have no opportunity for hydrogen bonding. With this modification, the infinite dilution activity coefficient expression (which can be compared with Equation 21 in Chapter 4) was

$$ \begin{aligned} \ln {}^{j}f_x^\infty = [{}^{j}V/(RT)][({}^{i}\delta_\lambda - {}^{j}\delta_\lambda)^2 &+ {}^{i}q^2 {}^{j}q^2 ({}^{i}\delta_\tau - {}^{j}\delta_\tau)^2/{}^{i}\psi \\ &+ ({}^{i}\delta_\alpha - {}^{j}\delta_\alpha)({}^{i}\delta_\beta - {}^{j}\delta_\beta)/ {}^{i}\xi] + {}^{ij}d \end{aligned} \tag{88} $$

where ${}^{ij}d$ is the Flory-Huggins combinatorial molecular size effect term (Section 13.2)

$$ {}^{ij}d = \ln({}^{j}V / {}^{i}V) + 1 - {}^{j}V / {}^{i}V \tag{89} $$

although in the correlation of Thomas and Eckert the "overcorrection" often caused by this form was largely avoided by using

$$ {}^{ij}d = \ln\,({}^{j}V / {}^{i}V)^{\,{}^{j}a} + 1 - ({}^{j}V / {}^{i}V)^{\,{}^{j}a} \tag{90} $$

where

$$ {}^{j}a = 0.953 - 0.00231\,({}^{j}\delta_\tau^2/\mathrm{MPa} + {}^{j}\delta_\alpha {}^{i}\delta_\beta\,/\mathrm{MPa}) \tag{91} $$

The parameters δ_τ, δ_α and δ_β were treated as being adjustable, with δ_λ calculated *a priori* from refractive index (Section 3.4). All the parameters necessary for calculation of limiting activity coefficients (and other thermodynamic properties) are collected in the publication by Thomas and Eckert[149] and its associated Supplementary Material. The cohesion parameters in Table 23 have been rounded to 2 or 3 significant figures, and refer to 20°C. The quantities V, δ_λ and q were treated as temperature-independent; the other parameters were temperature-dependent:

TABLE 23
Cohesion Parameters from the MOSCED Approach at 20°C

Liquid	*V* cm³ mol⁻¹	δ/MPa$^{1/2}$ δ_τ	δ_γ	δ_α	δ_β
Acetone	74.4	15.3	8.4	0.0	10.0
Acetonitrile	52.2	15.2	12.3	1.8	8.1
Acetophenone	116.9	18.0	6.2	1.8	6.4
Aniline	91.1	18.9	8.6	7.8	4.4
Anisole	108.1	17.7	5.7	0.6	3.3
Benzene	89.1	17.4	4.0	0.5	1.2
Benzonitrile	102.6	17.9	6.8	1.3	6.0
Benzyl acetate	142.4	17.8	6.7	0.5	5.1
Benzyl chloride	117.2	18.1	5.5	1.5	1.9
Bromoanisole	128.4	18.5	4.5	1.6	6.3
1-Bromobutane	107.4	17.1	3.1	0.5	0.4
Bromodichloromethane	82.7	18.3	4.1	5.9	0.2
Bromoethane	76.5	16.8	4.2	0.7	0.5
1-Bromohexadecane	305.6	17.6	1.4	0.2	0.1
Bromonaphthalene	149.6	20.0	4.0	1.2	0.8
1-Bromopentane	124.0	17.2	2.8	0.4	0.3
1-Bromopropane	90.9	17.0	3.6	0.6	0.4
Bromotrichloromethane	98.5	18.5	2.0	1.4	0.2
Butane	100.4	14.7	0.0	0.0	0.0
1-Butanol	91.5	16.2	2.1	9.5	9.5
2-Butanone, methyl ethyl ketone	89.6	15.8	6.7	0.0	8.3
Butyl acetate	132.0	16.1	4.5	0.0	5.2
Butylbenzene	156.0	17.2	2.0	0.1	0.8
tert-Butyl chloride	109.9	15.9	3.3	0.5	0.3
Butylcyclohexane	175.5	17.1	0.0	0.0	0.0
Carbon disulfide	72.0	20.0	0.6	0.6	0.3
Chlorobenzene	101.8	17.8	3.8	1.5	0.9
1-Chlorobutane	104.5	16.3	3.4	0.5	0.3
2-Chlorobutane	106.0	16.2	3.3	0.5	0.3
1-Chlorohexadecane	301.5	17.4	1.5	0.2	0.1
1-Chloropropane	88.1	16.0	3.9	0.6	0.4
Cycloheptane	121.3	17.2	0.0	0.0	0.0
Cyclohexane	108.1	16.8	0.0	0.0	0.0
Cyclohexanol	105.4	17.7	1.8	8.2	8.2
Cyclohexanone	103.6	17.3	6.2	0.0	9.9
Cyclohexene	101.4	17.3	0.6	0.0	0.5
Cyclooctane	134.4	17.5	0.0	0.0	0.0
Cyclopentane	94.1	16.4	0.0	0.0	0.0
Cyclopentanol	90.9	17.4	2.3	9.2	9.2
Decahydronaphthalene	154.0	18.0	0.0	0.0	0.0
Decane	194.9	16.5	0.0	0.0	0.0
Decanenitrile	186.9	16.9	4.6	0.3	6.5
1-Decanol	190.8	17.1	1.2	5.6	5.6
1-Decene	189.3	16.7	0.4	0.0	0.4
Dibromomethane	69.6	19.3	5.9	4.1	0.2
Dibutyl ketone	173.1	16.7	7.4	0.0	4.5
1,1-Dichloroethane	84.2	16.6	4.5	2.0	0.6
1,2-Dichloroethane	79.1	17.2	6.4	1.6	1.0
Dichloromethane	64.1	16.8	5.7	5.1	0.8
Diisobutyl ketone	176.6	16.5	3.3	0.0	4.9
1,4-Dioxane	84.2	16.5	6.8	0.0	8.5
2,2-Dimethylbutane	132.9	15.6	0.0	0.0	0.0
2,3-Dimethylbutane	130.3	15.7	0.0	0.0	0.0
N,N-Dimethylformamide	77.0	16.9	9.5	1.3	21.1
2,2-Dimethylpentane	148.7	15.9	0.0	0.0	0.0

TABLE 23 (continued)
Cohesion Parameters from the MOSCED Approach at 20°C

Liquid	V cm³ mol⁻¹	$\delta/\mathrm{MPa}^{1/2}$ δ_τ	δ_γ	δ_α	δ_β
2,4-Dimethylpentane	149.0	15.8	0.0	0.0	0.0
Dodecane	227.5	16.7	0.0	0.0	0.0
Dotriacontane	555.0	17.4	0.0	0.0	0.0
Eicosane	358.3	17.2	0.0	0.0	0.0
Ethanol	58.4	15.4	2.8	12.7	12.7
Ethyl acetate	97.8	15.6	5.8	0.0	6.7
Ethylbenzene	122.5	17.4	2.6	0.1	1.0
Ethyl butyl ketone	139.5	16.4	4.4	0.0	5.5
Ethylcyclohexane	142.4	17.0	0.0	0.0	0.0
Ethyl formate	80.4	15.3	6.8	0.0	7.8
Ethyl octanoate	143.6	18.5	3.2	0.0	3.7
Ethyl propionate	114.5	15.9	5.1	0.0	5.9
Heneicosane	374.6	17.2	0.0	0.0	0.0
Heptane	146.6	16.0	0.0	0.0	0.0
Heptanenitrile	137.2	16.7	5.9	0.5	4.1
1-Heptene	140.9	16.2	0.5	0.0	0.5
Hexadecane	292.8	17.0	0.0	0.0	0.0
1-Hexadecanol	288.0	17.3	0.9	4.1	4.1
Hexadecene	287.3	17.1	0.2	0.0	0.2
Hexane	130.8	15.7	0.0	0.0	0.0
1-Hexanol	124.7	16.7	1.7	7.6	7.6
1-Hexene	125.0	16.0	0.0	0.0	0.4
Iodoethane	93.6	18.7	3.4	0.6	0.6
Iodomethane	79.1	19.0	4.0	0.7	0.6
2-Iodopropane	111.6	18.1	2.9	0.3	0.3
Isooctane	165.1	16.0	0.0	0.0	0.0
Isopentane	116.4	15.2	0.0	0.0	0.0
Isopentene	105.9	16.0	0.5	0.0	0.4
Isoprene	100.0	16.7	1.1	0.0	0.7
Methanol	40.5	14.6	5.2	15.2	15.2
Methyl acetate	79.3	15.4	6.8	0.0	7.8
3-Methyl-1-butene[a]	107.8	14.8	0.5	0.0	0.4
3-Methyl-1-butene[a]	111.8	15.4	0.5	0.0	0.4
Methyl butyrate	113.7	16.0	5.1	0.0	5.9
Methylcyclohexane	124.4	16.8	0.0	0.0	0.0
Methylcyclopentane	112.4	16.5	0.0	0.0	0.0
3-Methylhexane	145.8	16.0	0.0	0.0	0.0
Methyl isopropyl ketone	107.3	16.0	5.1	0.0	6.6
2-Methylpentane	131.9	15.6	0.0	0.0	0.0
3-Methylpentane	129.7	15.7	0.0	0.0	0.0
4-Methyl-2-pentanone	125.1	16.1	5.0	0.0	6.1
2-Methyl-1-pentene	126.7	15.9	0.5	0.0	0.4
2-Methyl-2-pentene	122.6	16.3	0.5	0.0	0.4
4-Methyl-1-pentene	123.8	16.1	0.5	0.0	0.4
Methyl propionate	96.3	15.7	5.8	0.0	6.7
Nitrobenzene	102.3	18.3	7.7	1.3	2.8
Nitroethane	72.0	16.1	9.9	0.6	4.5
Nitromethane	53.7	15.8	12.8	2.7	4.9
1-Nitropropane	89.0	16.3	8.5	0.5	3.9
2-Nitropropane	90.1	16.1	8.5	0.5	3.8
Nonane	178.7	16.4	0.0	0.0	0.0
Octacosane	489.4	17.4	0.0	0.0	0.0
Octadecane	327.1	17.1	0.0	0.0	0.0
Octane	162.6	16.2	0.0	0.0	0.0
1-Octanol	157.8	16.9	1.4	6.4	6.4

TABLE 23 (continued)
Cohesion Parameters from the MOSCED Approach at 20°C

Liquid	V cm^3 mol^{-1}	δ/MPa$^{1/2}$			
		δ_τ	δ_γ	δ_α	δ_β
1-Octene	157.0	16.4	0.5	0.0	0.4
Palmitonitrile	286.0	17.2	3.3	0.2	2.3
trans-1,3-Pentadiene	100.8	16.9	1.2	0.0	0.8
Pentane	115.3	15.3	0.0	0.0	0.0
1-Pentanol	108.1	16.5	1.8	8.4	8.4
2-Pentanone, methy propyl ketone	106.5	16.0	5.7	0.0	7.0
3-Pentanone, diethyl ketone	105.8	16.1	5.7	0.0	7.0
Pentatriacontane	604.4	17.5	0.0	0.0	0.0
1-Pentene	109.6	15.6	0.5	0.0	0.4
2-Pentene	107.0	15.9	0.5	0.0	0.4
Phenol	89.0	18.3	4.4	33.1	3.4
Propane	88.1	13.7	0.0	0.0	0.0
1-Propanol	74.8	15.9	2.4	10.8	10.8
Propionitrile	70.4	15.5	9.9	0.8	6.8
Propiophenone	132.9	17.9	5.6	1.4	6.0
Propyl acetate	115.0	15.9	5.1	0.0	5.9
Propyl formate	97.3	15.7	5.8	0.0	6.7
Pyridine	80.5	17.5	6.5	1.4	13.7
Quinoline	118.1	19.6	5.7	0.7	6.3
Squalene	478.5	18.4	0.6	0.0	1.4
Tetrachloromethane	96.5	17.6	1.8	1.2	0.3
Tetracosane	423.8	17.3	0.0	0.0	0.0
Tetrahydrofuran	81.1	16.4	4.7	0.0	9.4
Toluene	106.3	17.3	3.2	0.3	1.2
Triacontane	522.2	17.4	0.0	0.0	0.0
1,1,1-Trichloroethane	99.6	17.1	2.9	1.0	0.4
1,1,2-Trichloroethane	92.7	17.8	4.9	3.1	0.4
Trichloromethane	80.7	17.2	4.0	6.2	0.1
Triethylamine	139.0	15.4	1.1	0.0	10.2
1,3,5-Trimethylcyclohexane	163.8	16.8	0.0	0.0	0.0
Tripropylamine	189.6	15.6	0.9	0.0	6.8
o-Xylene	120.6	17.6	3.4	0.1	1.8
p-Xylene	123.3	17.3	2.6	0.1	1.5

[a] Two entries reported in original publication.

Adapted from Thomas, E. R. and Eckert, C. A., *Ind. Eng. Chem. Proces. Des. Dev.*, 23, 194, 1984.

$$\delta_\tau(T) = (293/T)^{0.4}\,\delta_\tau(293)$$

$$\delta_\alpha(T) = (293/T)^{0.8}\,\delta_\alpha(293)$$

$$\delta_\beta(T) = (293/T)^{0.8}\,\delta_\beta(293)$$

Park and Carr[150] subsequently proposed that the original MOSCED assumption $\delta_\alpha = \delta_\beta$ for the alcohols be abandoned in favor of a more realistic evaluation. The method has been applied to extractive distillation (Section 7.10).

5.14 LIQUID METALS

Although the Hildebrand parameter concept has been applied to liquid metal miscibilities,[151,159,160,164] it appears[151] that incorporation of electronegativity differences is necessary to predict behavior. Kumar,[152] on the basis that the properties (particularly the degree of order) of liquid metals were closer to those of their solids than to their gaseous states, proposed that the much smaller enthalpies of fusion be used in place of enthalpies of vaporization to evaluate cohesion parameters, "Kumar parameters" (Table 24). As indicated in Section 2.2, the cohesion parameters calculated from the vaporization enthalpies of *solid* metals are not *Hildebrand* parameters, which are liquid-state properties. Similar values for other elements are listed in Table 4, Chapter 2. Table 25 reports internal pressures and cohesion parameters for liquid alkali metals from Shrivastava and Pandey[163] (Section 7.5).

Information on ionic liquids (molten salts) is included in Section 12.3.

for
een

TABLE 24
Hildebrand and Kumar Cohesion Parameters for Liquid Metals

Group	Element	Melting point, K	Electronegativity[a]	δ MPa$^{1/2}$	δ_K MPa$^{1/2}$
I A	Li	459	0.95	111	15.2
	Na	371	0.90	68	10.4
	K	336	0.81	43	7.2
	Rb	312	0.78	39	6.5
	Cs	301	0.76	33	5.5
II A	Be	1553	1.42	264	48.6
	Mg	923	1.16	102	25.3
	Ca	1123	1.03	82	18.3
	Sr	1043	0.99	70	17.2
	Ba	977	0.92	68	14.0
III A	Sc	1473	1.27	164	29.9
	Y	1763	1.20	147	32.7
	La	1099	1.17	129	20.5
IVA	Ti	2093	1.62	192	42.0
	Zr	2023	1.48	192	38.3
	Hf	1973	1.48	—	39.3
	Th	2073	1.36	174	30.5
VA	V	2008	1.85	243	55.9
	Nb	2686	1.77	260	49.8
	Ta	3269	1.77	278	47.6
VI A	Cr	2163	2.15	221	53.8
	Mo	2898	2.05	262	54.4
	W	3683	2.05	297	59.5
	U	1403	1.30	205	33.0
VII A	Mn	1518	1.69	194	44.5
VIII	Fe	1812	2.21	239	46.5
	Co	1768	2.26	258	51.0
	Ni	1728	2.24	254	51.7
	Ru	2773	2.12	284	55.8
	Rh	2239	2.12	264	51.3
	Pd	1827	2.08	209	44.5
	Ir	2727	2.10	284	55.4
	Pt	2047	2.07	248	46.5
Rare earths	Ce	1070	1.21	139	21.0
	Gd	1585	1.20	129	27.7
I B	Cu	1356	2.00	219	42.9
	Ag	1234	1.90	168	34.1
	Au	1336	2.30	190	34.8
II B	Zn	693	1.50	119	28.4
	Cd	594	1.55	92	21.6
	Hg	234	1.80	63	12.4
III B	Al	933	1.48	176	10.4
	Ga	303	1.62	151	21.8
	In	429	1.48	123	14.4
	Tl	573	1.46	100	15.7
IV B	Si	1703	1.82	180	65.0
	Ge	1231	1.77	156	48.5
	Sn	505	1.61	133	21.1
	Pb	600	1.56	104	16.2
V B	As	1087	2.04	135	28.2
	Sb	904	2.10	121	32.8
	Bi	544	1.78	98	22.6
VI B	Se	493	2.35	72	18.2
	Te	723	2.08	63	29.2

[a] Data from Mott, B. W., *J. Mater. Sci.*, 3, 424, 1968.

Adapted from Kumar, R., *J. Mater. Sci.*, 7, 1409, 1972.

TABLE 25
Internal Pressures and Cohesion Parameters for Liquid Alkali Metals

Metal	t/°C	π/MPa	$\pi^{1/2}$/MPa$^{1/2}$
Sodium	100	473	21.8
	150	528	23.0
	200	573	23.9
	221	591	24.3
	245	614	24.8
Potassium	70	241	15.5
	113	262	16.2
	163	291	17.0
	191	294	17.2
	229	313	17.7
	263	314	17.7
Cesium	35	139	11.8
	76	154	12.4
	122	168	13.0
	169	180	13.4
	207	189	13.8
	247	196	14.0
Rubidium	43	182	13.5
	84	198	14.1
	120	214	14.6
	179	234	15.3
	208	244	15.6
	245	254	16.0

Adapted from Shrivastava, S. N. and Pandey, J. D., *Acoust. Lett.*, 3, 219, 1980.

REFERENCES

1. **Karger, B. L., Snyder, L. R., and Horvath, C.,** *An Introduction to Separation Science,* John Wiley & Sons, New York, 1973.
2. **Snyder, L. R.,** Solvent selection for separation processes, in *Separation and Purification,* 3rd ed., Perry, E. S. and Weissberger, A., Eds., John Wiley & Sons-Interscience, New York, 1978, 25.
3. **Karger, B. L., Snyder, L. R., and Eon, C.,** An expanded solubility parameter treatment for classification and use of chromatographic solvents and adsorbents. Parameters for dispersion, dipole and hydrogen bonding interactions, *J. Chromatogr.,* 125, 71, 1976.
4. **Karger, B. L., Snyder, L. R., and Eon, C.,** Expanded solubility parameter treatment for classification and use of chromatographic solvents and adsorbents, *Analyt. Chem.,* 50, 2126, 1978.
5. **Keller, R. A., Karger, B. L., and Snyder, L. R.,** Use of the solubility parameter in predicting chromatographic retention and eluotropic strength, *Gas Chromatography 1970* (Proc. Int. Symp., *8*, Dublin, 1970), Stock, R., Ed., The Institute of Petroleum, London, 1971, 125.
6. **Keller, R. A. and Snyder, L. R.,** Relation between the solubility parameter and the liquid-solid solvent strength parameter, *J. Chromatogr. Sci.,* 9, 346, 1971.
7. **Schoenmakers, P. J.,** *Optimization of Chromatographic Selectivity: A Guide to Method Development* (Journal of Chromatography Library, Vol. 35), Elsevier, Amsterdam, 1986.
8. **Schoenmakers, P. J., Billiet, H. A., and De Galan, L.,** Solubility parameter as a tool in understanding liquid chromatography, *Chromatographia,* 15, 205 (English) and 387 (German), 1982.
9. **Hansen, C. M.,** *Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient. Importance in Surface Coating Formulation,* Doctoral Dissentation, Danish Technical Press, Copenhagen, 1967.
10. **Hansen, C. M.,** The three dimensional solubility parameter — key to paint component affinities. I. Solvents, plasticizers, polymers and resins, *J. Paint Technol.,* 39, 104, 1967.

11. **Hansen, C. M.,** The three dimensional solubility parameter — key to paint component affinities. II. Dyes, emulsifiers, mutual solubility and compatibility, and pigments, *J. Paint Technol.*, 39, 505, 1967.
12. **Hansen, C. M.,** On the application of the three dimensional solubility parameter concept to the prediction of mutual solubility and compatibility, *Skand. Tidskr. Färg Lack*, 13, 132, 1967.
13. **Hansen, C. M.,** The three dimensional solubility parameter and its use. I. Introduction and non-pigmented systems, *Skand. Tidskr. Färg Lack*, 14(2), 28, 1968.
14. **Hansen, C. M.,** The universality of the solubility parameter, *Ind. Eng. Chem. Prod. Res. Dev.*, 8, 2, 1969.
15. **Hansen, C. M.,** Characterization of surfaces by spreading liquids, *J. Paint Technol.*, 42, 660, 1970.
16. **Hansen, C. M.,** Solubility in the coatings industry, *Skand. Tidskr. Färg Lack*, 17, 69, 1971.
17. **Hansen, C. M.,** Surface dewetting and coatings performance, *J. Paint Technol.*, 44(570), 57, 1972.
18. **Hansen, C. M.,** Solvents for coatings, *Chemtech*, 2, 547, 1972.
19. **Hansen, C. M.,** Solvent selection by computer, in *Solvents Theory and Practice (Adv. Chem. Ser.* 124), Tess, R. W., Ed., American Chemical Society, Washington, D.C., 1973, chap. 4.
20. **Hansen, C. M.,** Solvents in water-borne coatings, *Ind. Eng. Chem. Prod. Res. Dev.*, 16, 266, 1977.
21. **Hansen, C. M.,** Some aspects of acid/base interactions, *Farbe Lack*, 83, 595, 1977.
22. **Hansen, C. M.,** Advances in the technology of solvents in coatings, *FATIPEC (Fed. Assoc. Tech. Ind. Peint. Vernis, Emaux Encres Impr. Eur. Cont.) Congr.*, 14, 97, 1978.
23. **Hansen, C. M.,** Some answered and unanswered questions about the solubility parameter, in *Macromolecular Solutions: Solvent-Polarity Relationships in Polymers* (Symp. Proc., Am. Chem. Soc., New York, 1981), Seymour, R. B. and Stahl, G. A., Eds., Pergamon, New York, 1982, 1; *Org. Coat. Plast. Chem.*, 45, 227, 1981.
24. **Hansen, C. M.,** Organic solvents in high solids and water-reducible coatings, *Prog. Org. Coat.*, 10, 331, 1982.
25. **Hansen, C. M. and Beerbower, A.,** Solubility parameters, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Standen, A., Ed., Interscience, New York, Suppl. Vol., 1971, 889.
26. **Hansen, C. M. and Pierce, P. E.,** Surface effects in coating processes, *Ind. Eng. Chem. Prod. Res. Dev.*, 13, 218, 1974.
27. **Skaarup, K.,** The three dimensional solubility parameter and its use. II. Pigmented systems, *Skand. Tidskr. Färg Lack*, 14(3), 45, 1968.
28. **Hansen, C. M. and Skaarup, K.,** The three dimensional solubility parameter — key to paint component affinities. III. Independent calculation of the parameter components, *J. Paint Technol.*, 39, 511, 1967.
29. **Hansen, C. M. and Skaarup, K.,** Aspects of the three-dimensional solubility parameter, *Dan. Kemi*, 48(6), 81, 1967.
30. **Hansen, C. M. and Wallström, E.,** On the use of cohesion parameters to characterize surfaces, *J. Adhesion*, 15, 275, 1983.
31. **Beerbower, A., Wu, P. L., and Martin, A.,** Expanded solubility parameter approach. I. Naphthalene and benzoic acid in individual solvents, *J. Pharm. Sci.*, 73, 179, 1984.
32. **Martin, A., Wu, P. L., and Beerbower, A.,** Expanded solubility parameter approach. II. *p*-Hydroxybenzoic acid and *p*-hydroxybenzoate in individual solvents, *J. Pharm. Sci.*, 73, 188, 1984.
33. **Hildebrand, J. H.,** Absence of outer non-bonding electrons in methyl groups affects solubility parameters, *Ind. Eng. Chem. Fundam.*, 17, 365, 1978.
34. **Hildebrand, J. H.,** An improvement in the theory of regular solutions, *Proc. Natl. Acad. Sci., U.S.A.*, 76, 6040, 1979.
35. **Beerbower, A. and Jensen, W. B.,** The HSAB principle and extended solubility theory, *Inorg. Chim. Acta*, 75, 193, 1983.
36. **van Arkel, A. E.,** Mutual solubility of liquids, *Trans. Faraday Soc.*, 42B, 81, 1946.
37. **Munafo, A., Buchmann, M., Hô Nam-Tran, and Kesselring, U. W.,** Determination of the total and partial cohesion parameters of lipophilic liquids by gas-liquid chromatography and from molecular properties, *J. Pharm. Sci.*, 77, 169, 1988.
38. **Arnett, E. M.,** Quantitative comparison of weak organic bases, *Progr. Phys. Org. Chem.*, 1, 223, 1963.
39. **Bent, H. A.,** Structural chemistry of donor-acceptor interactions, *Chem. Rev.*, 68, 587, 1968.
40. **Bent, H. A.,** The nature of intermolecular donor-acceptor bonds, in *Solutions and Solubilities*, Part II, Dack, M. R. J., Ed., John Wiley & Sons-Interscience, New York, 1976, chap. 10.
41. **Coetzee, J. F. and Ritchie, C. D., Eds.,** *Solute-Solvent Interactions*, Marcel Dekker, New York, 1969.
42. **Drago, R. S.,** Quantitative evaluation and prediction of donor-acceptor interactions, *Struct. Bonding (Berlin)*, 15, 73, 1973.
43. **Drago, R. S. and Matwiyoff, N. A.,** *Acids and Bases*, Heath, Lexington, Mass., 1968, 66.
44. **Jensen, W. B.,** The Lewis acid-base definitions: a status report, *Chem. Rev.*, 78, 1, 1978.
45. **Jensen, W. B.,** Lewis acid-base interactions and adhesion theory, *Rubber Chem. Technol.*, 55, 881, 1982.
46. **Jensen, W. B.,** Acids, bases, and adhesion: a synergy, *Chemtech*, 12, 755, 1982.

47. **Lim, Y. Y. and Drago, R. S.,** Lewis acidity of antimony pentachloride, *Inorg. Chem.*, 11, 202, 1972.
48. **Reichardt, C.,** *Solvent Effects in Organic Chemistry,* (Monographs in Modern Chemistry, Vol. 3), Verlag Chemie, Weinheim, 1979.
49. **Wrona, P. K.,** On the correlation between empirical Lewis acid-base solvent parameters and the thermodynamic parameters of ion solvation, *J. Electroanal. Chem.*, 108, 153, 1980.
50. **Burrell, H.,** The challenge of the solubility parameter concept, *J. Paint Technol.*, 40, 197, 1968.
51. **Gardon, J. L.,** The influence of polarity upon the solubility parameter concept, *J. Paint Technol.*, 38(492), 43, 1966.
52. **Makitra, R. G. and Pirig, Ya. N.,** Interdependence between the basicity of donor solvents and heats of their mixing with chloroform, *Ukr. Khim. Zh. (Russ. Ed.)*, 46, 83, 1980.
53. **Nelson, R. C., Hemwall, R. W., and Edwards, G. D.,** Treatment of hydrogen bonding in predicting miscibility, *J. Paint Technol.*, 42, 636, 1970.
54. **Sörensen, P.,** New aspects on the application of the solubility parameters, *Skand. Tidskr. Färg Lack*, 20(2), 9, 1974.
55. **Sörensen, P.,** Application of the acid/base concept describing the interaction between pigments, binders and solvents, *J. Paint Technol.*, 47(602), 31, 1975.
56. **Benesi, H. A. and Hildebrand, J. H.,** A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons, *J. Am. Chem. Soc.*, 71, 2703, 1949.
57. **Alley, S. K., Jr. and Scott, R. L.,** NMR studies of hydrogen bonding in hydrofluorocarbon solutions, *J. Phys. Chem.*, 67, 1182, 1963.
58. **Pimentel, G. C. and McClellan, A.,** *The Hydrogen Bond,* W. H. Freeman, San Francisco, 1960.
59. **Burrell, H.,** Trends in solvent science and technology, in *Solvents Theory and Practice (Adv. Chem. Ser.* 124), Tess, R. W., Ed., American Chemical Society, Washington, D.C., 1973, chap. 1.
60. **Small, P. A.,** Some factors affecting the solubility of polymers, *J. Appl. Chem.*, 3, 71, 1953.
61. **Rider, P. E.,** A two-parameter model for estimating hydrogen bond enthalpies of reaction, *J. Appl. Polym. Sci.*, 25, 2975, 1980; Hydrogen bonding potential, HBP: A model for predicting resin solubilities in organic solvent, *Polym. Eng. Sci.*, 23, 810, 1983.
62. **Rider, P. E.,** Theories of solvency and solution, in *Applied Polymer Science,* 2nd ed., Vol. 285, Tess, R. W. and Poehlein, G. W., Eds., 1985, chap. 27, 643.
63. **Chastrette, M., Rajzmann, M., Chanou, M., and Purcell, K. F.,** Approach to a general classification of solvents using a multivariate statistical treatment of quantitative solvent parameters, *J. Am. Chem. Soc.*, 107, 1, 1985.
64. **Renon, H. and Prausnitz, J. M.,** On the thermodynamics of alcohol-hydrocarbon solutions, *Chem. Eng. Sci.*, 22, 299, 1967.
65. **Wiehe, I. A. and Bagley, E. B.,** Estimation of dispersion and hydrogen bonding energies in liquids, *Am. Inst. Chem. Eng. J.*, 13, 836, 1967.
66. **Bagley, E. B. and Chen, S.-A.,** Hydrogen bonding effects in non-electrolyte solutions, *J. Paint Technol.*, 41, 494, 1969.
67. **Harris, H. G. and Prausnitz, J. M.,** Thermodynamics of solutions with physical and chemical interactions, *Ind. Eng. Chem. Fundam.*, 8, 180, 1969.
68. **Kirchnerova, J. and Cavé, G. C. B.,** The solubility of water in low-dielectric solvents, *Can. J. Chem.*, 54, 3909, 1978.
69. **Hoy, K. L.,** New values of the solubility parameters from vapor pressure data, *J. Paint Technol.*, 42(541), 76 and 115, 1970.
70. **Kojima, I., Yoshida, M., and Tanaka, M.,** Distribution of carboxylic acids between organic solvents and aqueous perchloric acid solution, *J. Inorg. Nucl. Chem.*, 32, 987, 1970.
71. **Takeda, K., Yamashita, H., and Akiyama, M.,** Dimerization of some carboxylic acids in organic phases, *Solvent Extr. Ion Exch.*, 5, 29, 1987.
72. **Iscan, M.,** Temperature effect on the partition and dimerization constant of benzoic acid, *Thermochim. Acta*, 94, 305, 1985.
73. **Martin, A., Wu, P. L., Liron, Z., and Cohen, S.,** Dependence of solute solubility parameters on solvent polarity, *J. Pharm. Sci.*, 74, 638, 1985.
74. **Kamlet, M. J., Doherty, R., Taft, R. W., and Abraham, M. H.,** Linear solvation energy relationships. 26. Some measures of relative self-association of alcohols and water, *J. Am. Chem. Soc.*, 105, 6741, 1983.
75. **Nisbet, K. D.,** Structure-solubility parameter relationships in alcohols, in *Structure-Solubility Relationships in Polymers* (Proc. Symp., 1976), Harris, F. W. and Seymour, R. B., Eds., Academic Press, New York, 1977, 33.
76. **Melder, L. I. and Ebber, A. V.,** Determination of the orientation and induction components of the solubility parameter of polar compounds without hydrogen bonds, *Zh. Prikl. Khim.*, 55, 1979, 1982; *J. Appl. Chem. U.S.S.R.*, 55, 1823, 1982.

77. **Melder, L. and Ebber, A.,** Use of the theory of regular solutions for the description of solutions with polar components without a hydrogen bond. 1. Selection of the method for the expression of polarizability of solution components in the calculation of induction interaction energy, *Tr. Tallin. Politekhn. In-ta,* No. 509, 3, 1981.
78. **Ebber, A.,** Use of the theory of regular solutions for the description of solutions with polar components without a hydrogen bond. 2. Determination of orientation and induction components of the solubility parameter, *Tr. Tallin. Politekhn. In-ta,* No. 509, 15, 1981.
79. **Melder, L. and Ebber, A.,** Splitting of the overall solubility parameter of polar solvents without hydrogen bonding into dispersion, orientation and induction components, *Eesti NSV Tead. Akad. Toim. Keem.,* 30(1), 39, 1981.
80. **Ignat, A. V. and Melder, L. I.,** Determination of components of the solubility parameter of alcohols, *Zh. Prikl. Khim. (Leningrad),* 60, 1136, 1987; *J. Appl. Chem. U.S.S.R.,* 60, 1070, 1987.
81. **Ignat, A. and Melder, L.,** Splitting the solubility parameter of self-associating compounds into components, *Eesti NSV Tead. Akad. Toim. Keem.,* 36(1), 45, 1987.
82. **Fedors, R. F.,** A method for estimating both the solubility parameters and molar volumes of liquids, *Jet Propul. Lab. Quart. Tech. Rev.,* 3(1), 45, 1973; *Polym. Eng. Sci.,* 14, 147 and 472, 1974.
83. **Walker, E. E.,** Solvent action of organic substances on polyacrylonitrile, *J. Appl. Chem.,* 2, 470, 1952.
84. **Reed, T. M., III,** The theoretical energies of mixing for fluorocarbon-hydrocarbon mixtures, *J. Phys. Chem.,* 59, 425, 1955.
85. **Reed, T. M., III,** The polarizabilities of molecules in liquid mixtures, *J. Phys. Chem.,* 63, 1798, 1959.
86. **Sonnich Thomsen, E.,** *The Energy of Mixing of Non-Polar Liquids. Reflections upon the Hildebrand Theory,* Thesis, Royal Danish School of Pharmacy, Copenhagen, 1965.
87. **Sonnich Thomsen, E.,** The energy of mixing of non-polar liquids. Reflections upon the theories of Prigogine and Hildebrand, *Dansk Kemi,* 47(3), 35, 1966.
88. **Sonnich Thomsen, E.,** Interactions between unlike nonpolar molecules: correction of the geometric mean rule. 1. Basic derivations; 2. Dilute systems; 3. Energies of mixing, *Acta Chem. Scand.,* 25, 260 and 265, 1971; 26, 2100, 1972.
89. **Reid, R. C., Prausnitz, J. M., and Sherwood, T. K.,** *The Properties of Gases and Liquids,* McGraw-Hill, New York, 3rd ed., 1977.
90. **Preston, G. T. and Prausnitz, J. M.,** Thermodynamics of solid solubility in cryogenic solvents, *Ind. Eng. Chem. Process Des. Dev.,* 9, 264, 1970.
91. **Funk, E. W. and Prausnitz, J. M.,** Thermodynamic properties of liquid mixtures: aromatic — saturated hydrocarbon systems, *Ind. Eng. Chem.,* 62(9), 8, 1970.
92. **Bazua, E. R. and Prausnitz, J. M.,** Vapour-liquid equilibria for cryogenic mixtures, *Cryogenics,* 11, 115, 1971.
93. **Utracki, L. A.,** Interactions in poly(vinyl chloride) solutions, *Polym. J.,* 3, 551, 1972.
94. **Martin, A., Newburger, J., and Adjei, A.,** New solubility equation, *J. Pharm. Sci.,* 68(10), iv, 1979.
95. **Martin, A., Newburger, J., and Adjei, A.,** Extended Hildebrand solubility approach. II. Solubility of theophylline in polar binary solvents, *J. Pharm. Sci.,* 69, 487, 1980.
96. **Adjei, A., Newburger, J., and Martin, A.,** Extended Hildebrand approach. III. Solubility of caffeine in dioxane-water mixtures, *J. Pharm. Sci.,* 69, 659, 1980.
97. **Martin, A., Wu, P. L., Adjei, A., Mehdizadeh, M., James, K. C., and Metzler, C.,** Extended Hildebrand solubility approach: testosterone and testosterone propionate in binary solvents, *J. Pharm. Sci.,* 71, 1334, 1982.
98. **Martin, A., Paruta, A. N., and Adjei, A.,** Extended Hildebrand solubility approach: methylxanthines in mixed solvents, *J. Pharm. Sci.,* 70, 1115, 1981.
99. **Li, Y.-G., Teng, T., Lu, J.-F., Chen, G., and Li, J.-D.,** A study on Scatchard-Hildebrand solution theory for metal solvent extraction systems, *Fluid Phase Equil.,* 30, 297, 1986.
100. **James, K. C., Ng, C. T., and Noyce, P. R.,** Solubilities of testosterone propionate and related esters in organic solvents, *J. Pharm. Sci.,* 65, 656, 1976.
101. **Chueh, P. L. and Prausnitz, J. M.,** Vapor-liquid equilibrium at high pressures. Vapor-phase fugacity coefficients in nonpolar and quantum gas mixtures, *Ind. Eng. Chem. Fundam.,* 6, 492, 1967.
102. **Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L.,** *Regular and Related Solutions,* Van Nostrand-Reinhold, Princeton, NJ, 1970.
103. **Knobler, C. M.,** Volumetric properties of gaseous mixtures, *Chem. Soc. Spec. Per. Rep. Chem. Thermodyn.,* 2, 199, 1978.
104. **Prausnitz, J. M. and Chueh, P. L.,** *Computer Calculations for High Pressure Vapor Equilibria,* Prentice-Hall, Englewood Cliffs, NJ, 1966.
105. **Sonnich Thomsen, E.,** Present state of the solubility parameter theory, *Mitt. Chem. Gesell. DDR,* 16, 150, 1969.
106. **Pauling, L.,** *The Nature of the Chemical Bond,* 3rd ed., Cornell University Press, Ithaca, NY, 1960.
107. **Stringfellow, G. B.,** The calculation of regular solution interaction parameters between elements from Groups III, IV and V of the Periodic Table, *Mater. Res. Bull.,* 6, 371 and 639, 1971.

108. **Myers, A. L. and Prausnitz, J. M.,** Thermodynamics of solid carbon dioxide solubility in liquid solvents at low temperatures, *Ind. Eng. Chem. Fundam.*, 4, 209, 1965.
109. **Andersen, R.,** Ph.D. Thesis, Dept. of Chemical Engineering, University of California, Berkeley, 1961.
110. **Blanks, R. F. and Prausnitz, J. M.,** Thermodynamics of polymer solubility in polar and nonpolar systems, *Ind. Eng. Chem. Fundam.*, 3, 1, 1964.
111. **Kumar, R. and Prausnitz, J. M.,** Solvents in chemical technology, in *Solutions and Solubilities*, Part 1, Dack, M. R. J., Ed., John Wiley & Sons-Interscience, New York, 1975, chap. 5.
112. **Prausnitz, J. M. and Anderson, R.,** Thermodynamics of solvent selectivity in extractive distillation of hydrocarbons, *Am. Inst. Chem. Eng. J.*, 7, 96, 1961.
113. **Weimer, R. F. and Prausnitz, J. M.,** Screen extraction solvents this way, *Hydrocarbon Proc. Petr. Ref.*, 44, 237, 1965.
114. **Prausnitz, J. M. and Shair, F. H.,** A thermodynamic correlation of gas solubilities, *Am. Inst. Chem. Eng. J.*, 7, 682, 1961.
115. **Helpinstill, J. G. and Van Winkle, M.,** Prediction of infinite dilution activity coefficients for polar-polar binary systems, *Ind. Eng. Chem. Proc. Des. Dev.*, 7, 213, 1968.
116. **Seidel, P. and Bittrich, H.-J.,** The polar contribution to the heat of vaporization, *Chem. Tech.*, 36, 382, 1984.
117. **Böttcher, C. J. F.,** *Theory of Electric Polarisation*, Elsevier, New York, 1952.
118. **Beerbower, A. and Dickey, J. R.,** Advanced methods for predicting elastomer/fluids interactions, *Am. Soc. Lubric. Eng. Trans.*, 12, 1, 1969.
119. **Gardon, J. L. and Teas, J. P.,** Solubility parameters, in *Treatise on Coatings*, Vol. 2, Part II, Myers, R. R. and Long, J. S., Eds., Marcel Dekker, New York, 1976, chap. 8, 413.
120. **Beerbower, A.,** Surface free energy: a new relationship to bulk energies, *J. Colloid Interface Sci.*, 35, 126, 1971.
121. **Izumi, Y. and Miyake, Y.,** Study of linear poly(*p*-chlorostyrene)-diluent systems. I. Solubilities, phase relationships, and thermodynamic interactions, *Polym. J.*, 3, 647, 1972.
122. **Knox, B. H.,** Bimodal character of polyester-solvent interactions. I. Evaluation of the solubility parameters of the aromatic and the aliphatic ester residues of poly(ethylene terephthalate), *J. Appl. Polym. Sci.*, 21, 225, 1977.
123. **Brench, A.,** unpublished presentation, *Soc. Chem. Ind. Symp.*, 1978 (cited in Ref. 124).
124. **Ashton, N. F., McDermott, C., and Brench, A.,** Chemistry of extraction of nonreacting solutes, in *Handbook of Solvent Extraction*, Lo, T. C., Baird, M. H. I., and Hanson, C., Eds., John Wiley & Sons-Interscience, New York, 1983, 3.
125. **Stephanopoulos, G. and Townsend, D. W.,** Synthesis in process development, *Chem. Eng. Res. Des.*, 64, 160, 1986.
126. **Hoy, K. L.,** *Tables of Solubility Parameters*, Union Carbide Corporation, Chemicals and Plastics Research and Development Dept., South Charleston, WV, 1969, 1975, and 1985.
127. **Grunwald, E. G.,** Thermodynamic properties of nonpolar solutes in water and the structure of hydrophobic hydration shells, *J. Am. Chem. Soc.*, 108, 5726, 1986.
128. **Tawn, A. R. H.,** Discussion following paper by K. Skaarup, *Skand. Tidskr. Färg Lack*, 15, 52, 1968.
129. **Teas, J. P.,** Graphic analysis of resin solubilities, *J. Paint Technol.*, 40(516), 19, 1968.
130. **Vial, J.,** Tridimensional representation of the solubility parameters: study of the solubilization of a vinyl chloride-vinyl acetate copolymer, *Compt. Rend. Acad. Sci. Ser. C*, 270, 683, 1970.
131. **Vial, J.,** *Predicting the Solubility of Polymers: Application to some Vinyl Chloride-Vinyl Acetate Copolymers*, Thesis, Faculty of Science, Paris, 1970.
132. **Teas, J. P.,** *Predicting Resin Solubilities*, Ashland Chemical Co., Tech. Bull. 1206, Ashland Chemical Co., Ashland, KY, 1971.
133. **Peiffer, D.,** The molecular factors affecting the solubility parameter, *J. Appl. Polym. Sci.*, 25, 369, 1980.
134. **Null, H. R.,** *Phase Equilibrium in Process Design*, John Wiley & Sons-Interscience, New York, 1970.
135. **Null, H. R. and Palmer, D. A.,** Predicting phase equilibria, *Chem. Eng. Prog.*, 65(9), 47, 1969.
136. **Wiehe, I. A.,** *Thermodynamics of Alcohol-Inert Solvent Solutions*, Thesis, Washington University, St. Louis, MO, 1967; *Diss. Abstr. B*, 28, 166, 1967.
137. **Wiehe, I. A.,** Thermodynamic properties of solutions of alcohols in inert solvents, *Ind. Eng. Chem. Fundam.*, 6, 209, 1967.
138. **Lille, Ü., Kundel, H., and Eisen, O.,** Solubility parameters of alkyl derivatives of phenol and resorcinol, *J. Chromatogr.*, 116, 1, 1976.
139. **Stelkol'shchikov, M. N., Krivtsova, L. M., and Ratner, M. I.,** Evaluation of solvency of hydrocarbon solvents, *Khim. Tekhnol. Topl. Masel*, No. 6, 33, 1987; *Chem. Technol., Fuels Oils*, No. 6, 292, 1987.
140. **Martin, A., Wu, P. L., Adjei, A., and Beerbower, A.,** Extended Hansen solubility approach — naphthalene in individual solvents, *J. Pharm. Sci.*, 70, 1260, 1981.
141. **Wu, P. L., Beerbower, A., and Martin, A.,** Extended Hansen solubility approach — calculating partial solubility parameters of solid solutes, *J. Pharm. Sci.*, 71, 1285, 1982.

142. **Mogensen, O. E.,** Information on the structure of liquids and solutions obtained by positron annihilation, *Electrochim. Acta,* 33, 1203, 1988.
143. **Kamlet, M. J., Abboud, J. L. M., and Taft, R. W.,** An examination of linear solvation energy relationships, in *Progress in Physical Organic Chemistry,* Vol. 13, Taft, R. W., Ed., John Wiley & Sons, New York, 1981, 485.
144. **Karim, K. A. and Bonner, D. C.,** Thermodynamic interpretation of solute-polymer interactions at infinite dilution, *J. Appl. Polym. Sci.,* 22, 1277, 1978; erratum, *J. Appl. Polym. Sci.,* 23, 2825, 1979.
145. **Karim, K. A. and Bonner, D. C.,** An improved concept in solubility theory applied to amorphous polymers. I. Poly(ethyl methacrylate), *Polym. Eng. Sci.,* 19, 1174, 1979.
146. **Wingefors, S.,** *Studies of the Solvent Extraction Chemistry of Dialkyldithiophosphates and Development of Models for Non-Ideal Behavior in Solvent Extraction,* Thesis, Dept. of Nuclear Chemistry, Chalmers University of Technology, Göteborg, Sweden, 1979.
147. **Wingefors, S., Liljenzin, J. O., and Saalman, E.,** Three-dimensional solubility parameters for the correlation and prediction of liquid-liquid partition constants of metal chelate complexes, *Proc. Int. Solvent Extr. Conf.,* 3, Paper 8-116, 1980.
148. **Bagley, E. B., Nelson, T. P., and Scigliano, J. M.,** Three-dimensional solubility parameters and their relationship to internal pressure measurements in polar and hydrogen bonding solvents, *J. Paint Technol.,* 43(555), 35, 1971.
149. **Thomas, E. R. and Eckert, C. A.,** Prediction of limiting activity coefficients by a modified separation of cohesive energy density model and UNIFAC, *Ind. Eng. Chem. Process Des. Dev.,* 23, 194, 1984.
150. **Park, J. H. and Carr, P. W.,** Predictive ability of the MOSCED and UNIFAC activity coefficient estimation methods, *Analyt. Chem.,* 59, 2596, 1987.
151. **Mott, B. W.,** Liquid immiscibility in metal systems, *Phil. Mag.,* [8], 2, 259, 1957; Immiscibility in liquid metals systems, *J. Mater. Sci.,* 3, 424, 1968.
152. **Kumar, R.,** Clusters in liquid metals, *Contemp. Phys.,* 10, 49, 1969; Immiscibility in binary alloys of group 1B metals (copper, silver and gold) — a semi-empirical approach, *J. Mater. Sci.,* 7, 1409, 1972.
153. **Huyskens, P. L., Haulait-Pirson, M. C., Siegel, G. G., and Kapuku, F.,** Gibbs energy of some binary systems containing hydrogen bonds, *J. Phys. Chem.,* 92, 6841, 1988; **Huyskens, P. L. and Siegel, G. G.,** Fundamental questions about entropy, *Bull. Soc. Chem. Belg.,* 97, 809, 815, 821, and 825, 1988.
154. **Huyskens, P. L.,** Prediction of the dissolving power of pure solvents for crystalline substances and drugs, 3rd Cycle Course in Pharmaceutical Sciences, Champéry, Switzerland, October 1989.
155. **Hansen, C. M. and Andersen, B. H.,** The affinities of organic solvents in biological systems, *Am. Ind. Hyg. Assoc.,* 49, 301, 1988.
156. **Dickerson, C. G. and Wiehe, I. A.,** Spherical encapsulated polymer particles by spray drying, *Pac. Chem. Eng. Congr. [Proc.],* 2(1), 243, 1977.
157. **Kramer, A. and Thodos, G.,** Adaptation of the Flory-Huggins theory for modeling supercritical solubilities of solids, *Ind. Eng. Chem. Res.,* 27, 1506, 1988.
158. **Wakahayashi, T., Oki, S., Omori, T., and Suzuki, N.,** Some applications of the regular solution theory to solvent extraction — I. Distribution of β-diketones, *J. Inorg. Nucl. Chem.,* 26, 2255, 1964.
159. **Bowersox, D. F.,** Thermodynamic properties of selected solutes in liquid metal solutions, *U.S. A. E. C.,* CONF-690801, 565-75, 1969.
160. **Yatsenko, S. P. and Dieva, E. N.,** Solubility of high-melting metals in molten indium, *Zh. Fiz. Khim.,* 47, 2948, 1973; *Russ. J. Phys. Chem.,* 47, 1658, 1973.
161. **Ignat, A. and Melder, L.,** Determination of components of the solubility parameter of polar solvents, *Kh. Prikl. Khim. (Leningrad),* 62, 419, 1989; *J. Appl. Chem. U.S.S.R.,* 62, 376, 1989.
162. **Huyskens, P. L.,** Differences in the structures of highly polar and hydrogen-bonded liquids, *J. Mol. Struct.,* 198, 123, 1989.
163. **Shrivastava, S. N. and Pandey, J. D.,** Excess intermolecular free length and molecular interaction for binary molten metal halide and cryogenic liquid mixtures, *Acoust. Lett.,* 3, 219, 1980.
164. **Martin, B. G.,** Calculation of component partial pressures in the Hg-Te and Cd-Te binary systems using regular associated solution theory, *Bull. Am. Phys. Soc.,* 25, 349, 1980.
165. **Mikos, A. G. and Peppas, N. A.,** Flory interaction parameter χ for hydrophilic copolymers with water, *Biomaterials,* 9, 419, 1988.

m annihilation,

on energy rela-
Wiley & Sons,

tions at infinite
.979.
hous polymers.

d Development
stry, Chalmers

meters for the
oc. Int. Solvent

ieters and their
Paint Technol.,

fied separation
194, 1984.
cient estimation

ibility in liquid

inary alloys of
, 1409, 1972.
of some binary
.. and Siegel,
and 825, 1988.
ces and drugs,

ems, Am. Ind.

g, Pac. Chem.

ical solubilities

solution theory
964.
U.S. A. E. C.,

h. Fiz. Khim.,

r solvents, Kh.

'. Mol. Struct.,

interaction for

systems using

ers with water,

Chapter 6

CALCULATED COHESION PARAMETERS

Many properties of materials change in regular ways with increasing chain length in a homologous series, and some properties are conveniently linear. Thus, the logarithms of partition coefficients for some solutes between two liquids change linearly with chain length,[1] and a correlation exists[2] between methylene group increment and liquid Hildebrand parameter in octane-polar liquid systems (see Section 7.11). From the information presented in previous chapters, it is apparent that the miscibility behavior of materials depends to a large extent on two properties, the molar cohesive energy, $-U$, and the molar volume, V. Therefore, it is instructive to consider how $-U$, V, and the ratio and product of these two quantities vary through homologous series of organic compounds as chain lengths change, and how they can be estimated by means of contributions from groups of atoms.

Reference should also be made to Section 14.8 for additional sets of data, not only for polymer systems but also for materials such as long-chain lipophilic liquids with cohesion parameters that can be assessed in similar ways.[3]

6.1 GROUP MOLAR VAPORIZATION ENTHALPY

Dunkel[4] demonstrated 60 years ago that liquid molar vaporozation enthalpies at a given temperature could be estimated by the summation of atomic or group contributions, ${}^z\Delta H$:

$$\Delta H = \sum_z {}^z\Delta H \tag{1}$$

This approach (Table 1) was followed up by several investigators, including Hayes[5] and Fedors,[6] while Bondi[7,8] estimated the contributions to the enthalpy of vaporization extrapolated to absolute zero. Stein[9] also applied additive estimation methods to vaporization properties.

6.2 GROUP MOLAR COHESIVE ENERGY

It follows from the close relationship betwwen ΔH and $-U$ (Section 2.1) that the molar cohesive energy also increases in an approximately linear fashion with chain length in homologous series of compounds, and that group contribution methods may be used.[4,10-13] The lines obtained when $-U$ is plotted against chain length for molecules containing different functional groups are not quite parallel, and for accurate results in the use of group contributions the slopes of the lines have to be considered:[14]

$$-{}^zU = n\,{}^z\mu + {}^z\epsilon \tag{2}$$

where n is the number of carbon atoms, ${}^z\epsilon$ is the group molar cohesive energy constant, and ${}^z\mu$ is the chain length correction factor. Table 2 lists the values of these parameters for several groups. The molar cohesive energy is

$$-U = -\sum_z {}^zU \tag{3}$$

and the Hildebrand parameters may be calculated from

TABLE 1
Group Contributions to the Molar Vaporization Enthalpy[4,6]

Atom or group, z	${}^z\Delta H$/kJ mol^{-1}
$-CH_3$	7.45
$=CH_2$	7.45
$-CH_2-$	4.14
$=CH-$	4.14
$>CH-$	−1.59
$-O-$	6.82
$-OH$	30.3
$=CO$	17.9
$-CHO-$	19.7
$-COOH$	37.5
$-COOCH_3$	23.4
$-COOC_2H_5$	26.1
$-NH_2$	14.8
$-Cl$	14.2
$-F$	8.6[a]
$-Br$	18.0[a]
$-I$	21.1[a]
$-NO_2$	30.1[a]
$-SH$	17.8[a]

[a] Provisional value.

TABLE 2
Group Molar Cohesive Energies, Molar Volumes, and Attraction Constants at 25°C

Group, z	${}^z\epsilon$/kJ mol^{-1}	${}^z\mu$/kJ mol^{-1}	${}^zV$/cm^{3}mol^{-1}	${}^zF$/J$^{1/2}$cm$^{3/2}$ mol^{-1}
$>CH-$	4.06	0.0	−0.5	121
$-CH_2-$	5.15	0.0	16.5	286
$-CH_3$	4.14	0.0	34.0	405
$-CH{=}CH_2$	8.37	0.0	44.0	610
$-CH(CH_3)_2$	12.3	0.0	67.5	931
$-NH_2$	10.8	−0.38	19.0	477
$-Cl$	11.7	−0.25	24.0	497
$-CHO$	18.2	−0.71	26.0	710
CH_3COO-	23.2	−0.42	50.5	1105
Cyclohexyl	29.5	−0.92	95.0	1606
Phenyl	31.2	−0.92	75.0	1493
$-OH$	32.8	−0.34	8.7	908
$-COOH$	32.8	+0.92	27.0	1352[a]

[a] More correctly, 1113 + 80*n*.

Adapted from Rheineck, A. E. and Lin, K. F., *J. Paint Technol.*, 40, 611, 1968.

$$\delta = (-U/V)^{1/2} = \left(-\sum_z {}^zU \Big/ \sum_z {}^zV\right)^{1/2} \tag{4}$$

using group molar volumes (Section 6.5). This method requires knowledge of only the chemical structure, without the molar volume (or density), but it is applicable only at 25°C, and as presented in Table 2 is limited to 1-substituted *n*-alkanes because the dependence of

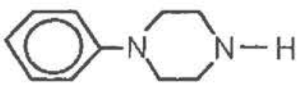
$^z\mu$ on chemical structure is not reported. The Hildebrand parameters of 1-substituted n-alkanes by this procedure are therefore given by

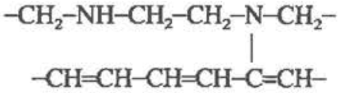
$$\delta = \left(\frac{^e\epsilon + {}^z\epsilon + (n - 1 + {}^z\mu)\,{}^u\epsilon}{^eV + {}^zV + (n - 1)\,{}^uV} \right)^{1/2} \tag{5}$$

for end-groups $e = -CH_3$ and repeat units $u = -CH_2-$. Also shown in Table 2 are the group molar attraction constants (Section 6.4),

$$\sum_z {}^zF = \left(-\sum_z {}^zU \sum_z {}^zV \right)^{1/2} = \delta V \tag{6}$$

Fedors[6] also has calculated molar vaporization energy contributions, $^z\Delta U$, and molar volume contributions, ^zV, for structural components (Table 3). Although it is considered[15] that they give less accurate estimates of cohesive energy than other sets of data, this compilation is noteworthy because of the great number of groups considered, and because of the inclusion of metals for use in calculations on organometallic compounds. Fedors found that it was possible to estimate both U and V (and therefore also δ) for cyclic compounds from the properties of linear compounds having the same structure, by means of a cyclization increment. For example, the liquid N-phenylpiperazine,
is considered as





$$\begin{array}{c} -CH_2-NH-CH_2-CH_2-N-CH_2- \\ \qquad\qquad\qquad\quad | \\ -CH{=}CH-CH{=}CH-C{=}CH- \end{array}$$

in which any functional group listed in Table 3 and present in the ring remains intact. Table 4 lists the group contributions, which result in an estimate for the Hildebrand parameter of 21.1 MPa$^{1/2}$. Kreibich and Batzer[16] used Fedors' cohesive energy increment values in an extensive study of polymer glass transition temperatures, while Sammar and Nagaka[103] applied the method to non-ionic surfactants.

It should be noted that when central atoms contain more than one substituent (other than the groups CH_3, CH_2, CH, or C) the contributions of those groups to the cohesive energy in Table 3 are decreased by approximately 20%, while the contributions to the molar volume are increased by about 7%.[6] Thus, in $CHCl_2$ the Cl contributions to $-U$ and V are -17% and $+8\%$, respectively, relative to the Cl contribution in CH_2Cl, while in $CHCl_3$ the figures are -34% and $+14\%$ relative to a single Cl substituent.

The increment of cohesion energy per $-CH_2-$ group would not be expected to be constant unless determined under conditions of constant reduced temperature (Section 7.3) rather than constant temperature. Meyer and co-workers[17-21] have done this in estimating the relative magnitudes of dispersion, induction, and orientation cohesive energies. A plot of cohesive energy against the number, m, of C–H bonds at the same reduced temperature for a homologous series of ketones was compared with a similar plot for alkanes (Figure 1). As the ketone alkyl chain length increases the orientation interactions decrease, the induction interactions are unaltered, and the dispersion interactions increase at the same rate as those for alkanes. At any m value, $-U_d$ is given by the alkane line, $-U_i$ is the vertical separation between the alkane line and the parallel line passing through the high-m ketone points, and

---

(4)

ɔnly the
at 25°C,
lence of

TABLE 3
Group Contributions to the Molar Vaporization Energy and Molar Volume at 25°C

Group, *z*	$^z\Delta U$/kJ mol^{-1}	^zV/cm^3 mol^{-1}
$-CH_3$	4.71	33.5
$-CH_2-$	4.94	16.1
$>CH-$	3.43	−1.0
$>C<$	1.47	−19.2
$H_2C=$	4.31	28.5
$-CH=$	4.31	13.5
$>C=$	4.31	−5.5
$HC\equiv$	3.85	27.4
$-C\equiv$	7.07	6.5
Phenyl	31.9	71.4
Phenylene (*o*, *m*, *p*)	31.9	52.4
Phenyl (trisubstituted)	31.9	33.4
Phenyl (tetrasubstituted)	31.9	14.4
Phenyl (pentasubstituted)	31.9	−4.6
Phenyl (hexasubstituted)	31.9	−23.6
Ring closure, 5 or more atoms	1.05	16
Ring closure, 3 or 4 atoms	3.14	18
Conjugation in ring, for each double bond	1.67	−2.2
Halogen attached to C atom with double bond	−20% of halogen $^z\Delta U$	
$-F$	4.19	18.0
$-F$ (disubstituted)	3.56	20.0
$-F$ (trisubstituted)	2.30	22.0
$-CF_2-$ (for perfluoro compounds)	4.27	23.0
$-CF_3-$ (for perfluoro compounds)	4.27	57.5
$-Cl$	11.55	24.0
$-Cl$ (disubstituted)	9.63	26.0
$-Cl$ (trisubstituted)	7.53	27.3
$-Br$	15.49	30.0
$-Br$ (disubstituted)	12.4	31.0
$-Br$ (trisubstituted)	10.7	32.4
$-I$	19.05	31.5
$-I$ (disubstituted)	16.7	33.5
$-I$ (trisubstituted)	16.3	37.0
$-CN$	25.5	24.0
$-OH$	29.8	10.0
$-OH$ (disubstituted or on adjacent C atoms)	21.9	13.0
$-O-$	3.35	3.8
$-CHO$ (aldehyde)	21.4	22.3
$-CO-$	17.4	10.8
$-CO_2-$	18.0	18.0
$-CO_3-$ (carbonate)	17.6	22.0
$-C_2O_3-$ (anhydride)	30.6	30.0
$HCOO-$ (formate)	18.0	32.5
$-CO_2CO_2-$ (oxalate)	26.8	37.3
$-HCO_3$	12.6	18.0
$-COF$	13.4	29.0
$-COCl$	17.6	38.1
$-COBr$	24.2	41.6
$-COI$	29.3	48.7
$-NH_2$	12.6	19.2
$-NH-$	8.4	4.5
$-N<$	4.2	−9.0
$-N=$	11.7	5.0

TABLE 3 (continued)
Group Contributions to the Molar Vaporization Energy and Molar Volume at 25°C

Group, z	${}^{z}\Delta U$/kJ mol^{-1}	${}^{z}V$/cm^3 mol^{-1}
–NHNH$_2$	22.0	—
–NNH$_2$	16.7	16
–NHNH	16.7	16
–N$_2$(diazo)	8.4	23
–N=N–	4.2	—
>C=N–N=C<	20.1	0
–N=C=N–	11.47	—
–NC	18.8	23.1
–NF$_2$	7.66	33.1
–NF–	5.07	24.5
–CONH$_2$	41.9	17.5
–CONH–	33.5	9.5
–CON<	29.5	−7.7
HCON<	27.6	11.3
HCONH–	44.0	27.0
–NHCOO–	26.4	18.5
–NHCONH–	50.2	—
–NHCON<	41.9	—
>NCON<	20.9	−14.5
NH$_2$COO–	37.0	—
–NCO	28.5	35.0
–ONH$_2$	19.1	20.0
>C=NOH	25.1	11.3
–CH=NOH	25.1	24.0
–NO$_2$ (aliphatic)	29.3	24.0
–NO$_2$ (aromatic)	15.36	32.0
–NO$_3$	20.9	33.5
–NO$_2$ (nitrite)	11.7	33.5
–NHNO$_2$	39.8	28.7
–NNO	27.2	10
–SH	14.44	28.0
–S–	14.15	12
–S$_2$–	23.9	23.0
–S$_3$–	13.40	47.2
>SO	39.1	—
SO$_3$	18.8	27.6
SO$_4$	28.5	31.6
–SO$_2$Cl	37.1	43.5
–SCN	20.1	37.0
–NCS	25.1	40.0
P	9.42	−1.0
PO$_3$	14.2	22.7
PO$_4$	20.9	28.0
PO$_3$(OH)	31.8	32.2
Si	3.4	0
SiO$_4$	21.8	20.0
B	13.8	−2.0
BO$_3$	0.0	20.4
Al	13.8	−2.0
Ga	13.8	−2.0
In	13.8	−2.0
Tl	13.8	−2.0
Ge	8.1	−1.5
Sn	11.3	1.5

TABLE 3 (continued)
Group Contributions to the Molar Vaporization Energy and Molar Volume at 25°C

Group, z	${}^z\Delta U$/kJ mol^{-1}	${}^zV$/cm^3 mol^{-1}
Pb	17.2	2.5
As	13.0	7.0
Sb	16.3	8.9
Bi	21.4	9.5
Se	17.2	16.0
Te	20.1	17.4
Zn	14.5	2.5
Cd	17.8	6.5
Hg	22.8	7.5

Adapted from Fedors, R. F., *J. Polym. Sci. C*, 26, 189, 1969, and van Krevelen, D. W., *Properties of Polymers*, 2nd ed., Elsevier, Amsterdam, 1976.

TABLE 4
Calculation of Hildebrand Parameter of N-Phenylpiperazine from Group Contributions

Group, z	$-{}^zU$/kJ mol^{-1} (Table 3)	$-\sum_z {}^zU$/kJ mol^{-1}	${}^zV$/cm^3 mol^{-1} (Table 3)	$\sum_z {}^zV$/cm^3 mol^{-1}
4(–CH$_2$–)	4.94	19.8	16.1	64.4
1(–NH–)	8.4	8.4	4.5	4.5
1(–N<)	4.2	4.2	−9.0	−9.0
5(–C=)	4.31	21.6	13.5	67.5
1(>C=)	4.31	4.3	−5.5	−5.5
3(Conjugated double bonds)	1.67	5.0	−2.2	−6.6
2(6-Membered rings)	1.05	2.1	16	32
		65.4		147

$$\delta = (65400/147)^{1/2} = 21.1 \text{ MPa}^{1/2}$$

Adapted from Fedors, R. F., *Polym. Eng. Sci.*, 14, 147 and 472, 1974.

$-U_o$ is given by the separation of the ketone curve from the straight line passing through the high-m points. (Figure 1 was derived on the basis of a $-CH_2-$ group molar volume of 19.08 cm^3 mol^{-1}, characteristic of hexane at 0°C. The temperature at which each member of the series displays 19.08 cm^3 per mole of $-CH_2-$ groups was calculated from thermal expansion data, and $-U$ was then calculated for each member at its own appropriate temperature. This plot therefore assumes a reduced temperature scale which differs from that based on the critical temperature.)

Lawson[22] has determined a set of group contributions to molar vaporization energy and molar volume for fluoro compounds, based on their boiling points and Equation 19, Chapter 7 (Table 5). Further information on cohesive energies has been presented by Polak,[23] Fried and Schneier,[24] and Maffiolo, Vidal, and Renon.[12] Group partial molal entropies, enthalpies, and Gibbs free energies of solution also have been used.[25-27]

6.3 MOLAR ADDITIVE FUNCTIONS

There is an important group of molar additive properties having the form[28]

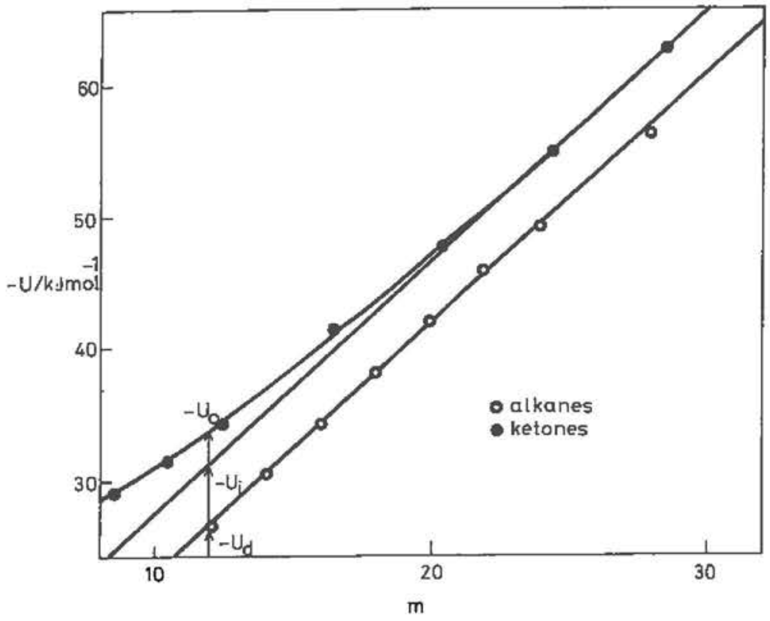


FIGURE 1. Molar cohesive energies as functions of C–H bond number for alkanes and ketones. (Adapted from Meyer, E. F. and Wagner, R. E., *J. Phys. Chem.*, 70, 3162, 1966.)

TABLE 5
Group Contributions to the Molar Vaporization Energy and Molar Volume at 25°C for Fluoro Compounds

Group, z	${}^{z}\Delta U$/kJ mol^{-1}	${}^{z}V$/cm^3 mol^{-1}
$-CF_3$	8.09	54.8
$-CF_2-$	3.28	23.1
–CFH–	1.77	18.6
–CF<	−1.66	−15.0
>C<(perfluoro)	−6.34	−38.3
>N–(perfluoro tertiary amine)	−3.82	−16.3
–O– (perfluoro ether)	0.03	19.0
5-Atom ring	8.46	37.7
6-Atom ring	9.51	39.9

Adapted from Lawson, D. D., *Appl. Energ.*, 6, 241, 1980.

$$Y = M\rho^{-1}f(x) = Vf(x) \tag{7}$$

where x is some physical quantity, including the molar parachor (Section 17.1), the lyoparachor (see below), molar attraction (Section 6.4), and molar refraction (Section 3.1).

In general, the group contributions ${}^{z}\Delta H$ are functions of temperature because ΔH itself is temperature dependent, but Bowden and Jones[29] showed that for a wide variety of both polar and nonpolar liquids it was possible to define constants related to ΔH and ΔU which are independent of temperature:

$$\frac{M}{{}^{l}\rho - {}^{g}\rho}\left(\frac{\Delta H}{M}\right)^{4/5} = [\mathrm{L}] \tag{8}$$

$$\frac{M}{{}^{l}\rho - {}^{g}\rho}\left(\frac{\Delta U}{M}\right)^{3/4} = [\Lambda] \tag{9}$$

The exponents 4/5 and 3/4 were determined empirically. The constants [L] and [Λ], termed the normal lyoparachor and true lyoparachor, respectively, are independent of temperature. For temperatures at or below the normal liquid boiling point, the vapor density ${}^{g}\rho$ is negligible compared with the liquid density ${}^{l}\rho$, so Equations 8 and 9 can be written

$$\Delta H = M([\mathrm{L}]/V)^{5/4} \tag{10}$$

$$\Delta U = M([\Lambda]/V)^{4/3} \tag{11}$$

It was found that both [L] and [Λ] could be obtained by summation of group constants:

$$[\mathrm{L}] = \sum_{z} {}^{z}[\mathrm{L}] \qquad [\Lambda] = \sum_{z} {}^{z}[\Lambda] \tag{12}$$

so the Hildebrand parameter can be expressed

$$\delta = \rho^{5/6}\left(\sum_{z} {}^{z}[\Lambda]/M\right)^{2/3} \tag{13}$$

Also, the temperature dependence of δ can be estimated from the temperature dependence of the density because the other factor is independent of temperature. Additional values have been provided by Wright[30] and the information on ^{z}[L] and ^{z}[Λ] has been collected by Fedors[6] (Table 6).

6.4 GROUP MOLAR ATTRACTION CONSTANTS

Scatchard[31] and Small[32] observed that there are parallel linear relationships among several homologous series when the square root of the product of the molar volume and molar cohesion energy, $(-UV)^{1/2}$, is plotted against the chain length (number of carbon atoms). In other words, $(-UV)^{1/2}$, or the equivalent quantity (δV), has additive properties. It has been described as the molar attraction, F (compare Equation 7),

$$F = \delta V \tag{14}$$

and can be considered to be made up of the sum of the group molar attraction constants ${}^{z}F$ of all the molecular groups z:

$$-U = \left(\sum_{z} {}^{z}F\right)^{2}/V \tag{15}$$

so

$$c = \left(\sum_{z} {}^{z}F/V\right)^{2} \tag{16}$$

and

$$\delta = \sum_{z} {}^{z}F/V = \sum_{z} {}^{z}F/\sum_{z} {}^{z}V \tag{17}$$

Molar cohesive energies and Hildebrand parameters can thus be estimated for any molecular compound once the individual group molar attraction constants are determined. Although

(9)

ıd [Λ], termed
ıf temperature.
ᶻρ is negligible

(10)

(11)

constants:

(12)

(13)

dependence
values have
d by Fedors[6]

ong several
and molar
atoms). In
It has been

(14)

ınstants ᶻF

(15)

(16)

(17)

ıolecular
Although

TABLE 6
Group Contributions to the Normal Lyoparachor, [L] and True Parachor, [Λ][6,29,30]

Group or atom, z	$^z[L]/J^{4/5}g^{1/5}$ cm^3 mol^{-1}	$^z[\Lambda]/J^{3/4}$ g$^{-3/4}$ cm^3 mol^{-1}
C	−3751	−2353
H	2655	1736
N	−354.2	−141.3
O (ether)	560.4	428.5
O (ketone)	6576	4403
O (ketone)[a]	6934	4601
O (carboxylate)	2840	1899
O (anhydride)[a]	4182	2796
O (carbonate)[a]	2074	1395
CN (aliphatic)[a]	7870	5294
CN (aromatic)[a]	6704	4543
Cl	2747	1881
Br	682.7	554
I	−54.1	118.5
Branch in a carbon chain	−417.1	−277.0
Benzene ring bonds	18190	11710
Cyclohexane ring bonds	3665	2322
Cyclohexene ring bonds[a]	8990	5754
O (carbonate)[b]	1729	1229
F[b]	1666	1112
Sn[b]	−4526	−2808
NO_2 (nitro)[b]	5280	3598
Double bond[b]	4620	2954
Double bond[a]	5249	3434
Triple bond[b]	11250	7342
Triple bond[a]	10510	6827
Pyridine ring bonds[b]	18540	12080
Furane ring bonds[b]	13390	8629

[a] From Reference 30 and the remainder from Reference 29.

[b] Provisional values.

the additivity of group molar attraction constants on an incremental basis is questionable on theoretical grounds, the method is adequate for many applications.[33,34] It provides acceptable data for hydrocarbons and many other compounds, but it is less satisfactory for situations where several large groups are packed around a central atom (as in tetrachloromethane, for example) and where steric, ring-closure, conjugation, polar, and hydrogen bonding effects are significant. (Small's values for group molar attraction constants at 25°C appear below in Table 11.)

Hoy[35,36] redetermined Small's constants on the basis of new values of Hildebrand parameters calculated from vapor pressure data for a large number of compounds. The Hildebrand parameters may be calculated from

$$\delta/\mathrm{MPa}^{1/2} = \left(\sum_z {}^zF + 276.3\right)/V \qquad (18)$$

In Table 7 are collected values of ^zF, together with the corresponding polar constants that are used in the same way to evaluate the polar cohesion parameter, δ_p (Section 5.9 and Section 6.8) and also the group molar volumes at the glass transition temperature.

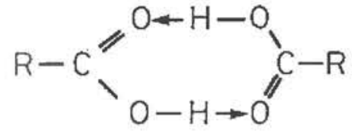
Numerical values of Hoy's cohesion parameters are presented in Table 18, Chapter 5,

TABLE 7
Hoy Group Molar Attraction Constants at 25°C

Group, z	Bond type	${}^zF/\mathrm{J}^{1/2}\,\mathrm{cm}^{3/2}\,\mathrm{mol}^{-1}$	${}^z\mathrm{F}_p/\mathrm{J}^{1/2}\,\mathrm{cm}^{3/2}\,\mathrm{mol}^{-1}$	${}^zV'\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$
Base value		276.3	—	—
–CH$_3$	Saturated	303.4	0.0	21.548
–CH$_2$–	Saturated	269.0	0.0	15.553
>CH–	Saturated	175.9	0.0	9.557
>C<	Saturated	65.5	0.0	3.562
CH$_2$=	Alkene	258.8	66.9	19.173
–CH=	Alkene	248.5	59.5	13.178
>C=	Alkene	172.8	63.0	7.183
–CH=	Aromatic	239.9	62.2	13.417
>C=	Aromatic	200.7	64.8	7.422
–O–	Ether	235.2	216.0	6.462
–O–	Acetal	236.3	10.2	6.462
–O–	Epoxide	360.4	155.9	6.462
–COO–	Ester	668.1	524.1	23.728
>C=O	Ketone	538.0	525.7	17.265
–CHO	Aldehyde	598.6	531.6	23.261
–(CO)$_2$O	Anhydride	1160.4	1159.8	40.993
–COOH	Acid	564.8	415.6	26.102
–OH→	H-bond OH	485.8	485.8	10.647
–OH	Primary (not H-bonded)	673.8	673.8	12.457
–OH	Secondary	591.6	591.6	12.457
–OH	Tertiary	798.6	798.6	12.457
–OH	Phenolic	349.8	349.8	12.457
–NH$_2$	Amino, primary	463.5	463.5	17.012
–NH–	Amino, secondary	368.2	368.2	11.017
>N–	Amino, tertiary	125.0	125.0	12.569
–C≡N	Nitrile	725.3	724.5	23.066
–NCO	Isocyanate	733.7	8.2	25.907
HCON<	Formamide	1017.0	724.1	35.830
–CONH–	Amide	1134.6	893.9	28.302
–CONH$_2$	Amide	1206.6	989.2	34.297
OCONH	Urethane	1261.9	892.2	34.784
–S–	Thioether	428.3	428.3	18.044
Cl	Primary	419.5	306.8	19.504
Cl	Secondary	426.1	315.0	19.504
Cl$_2$	Twinned	701.0	562.5	39.008
Cl	Aromatic	329.3	81.4	19.504
Br	Primary	527.5	122.7	25.305
Br	Aromatic	420.6	100.2	25.305
F	Primary	84.5	73.2	11.200
Conjugation		47.6	−19.8	—
Cis		−14.6	−14.5	—
Trans		−27.6	−27.6	—
4-Membered ring		159.1	200.5	—
5-Membered ring		42.9	84.9	—
6-Membered ring		−48.0	61.0	—
7-Membered ring		92.3	0.0	—
Bicycloheptane ring		46.2	—	—
Tricyclodecane ring		127.8	—	—
Ortho substitution		19.8	−13.3	—
Meta substitution		13.5	−24.3	—
Para substitution		82.4	−33.8	—

Adapted from Hoy, K. L., *The Hoy Tables of Solubility Parameters*, Union Carbide Corporation, 1975 and 1985; *J. Paint Technol.*, 42, 76, 1970.

which is based on the values in the 1975 and 1985 editions of the Union Carbide publication.[35,36] (The glycol ether values in the later editions have polar and nonpolar cohesion parameters that differ from those published earlier, a result of correcting a group value error.) Hoy found that the only compounds for which the simple molar attraction procedure was unsatisfactory were the acids, alcohols, and other compounds capable of association and ''chameleonic'' behavior (Section 5.5). He therefore took dimerization into account in such compounds:



If the cohesion parameter is expressed

$$\delta = (-U\rho/M)^{1/2} \tag{19}$$

then in the case of dimeric molecules the molar mass is $2M$, so

$$\delta = (-U\rho/2M)^{1/2} \tag{20}$$

Matsuura[37] used modified Small constants in a discussion of reverse osmosis separation. Another set of atomic attraction constants was derived by van Krevelen[38,39] based on the contributions of atoms and features such as double bonds (Table 8). This was intended for the investigation of coal (Section 16.11), but it was used by Chavan et al.[40] for anionic dyes (Section 17.8), and derived group attraction constants for polymers appear in Table 12, Chapter 14. In an interesting extension of the concept, molar attraction constants have been applied to the correlation of biological activity with chemical structure (Chapter 19). McGowan[41] estimated molecular attraction constants and cohesion parameters from characteristic atomic volumes.

It is not necessary to fully evaluate the Hildebrand parameter of a compound to benefit from information on group contribution values. Boberski, Seiner, and Petracca[42] have applied molar attraction constants to silicon chemistry, calculating a ''working Hildebrand parameter'' from a weighted average of individual carbon-based functional groups bonded to silicon (Section 17.5).

6.5 GROUP MOLAR VOLUME

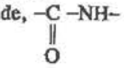
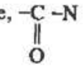
As indicated earlier in this chapter, the molar volumes of homologous series of molecules increase approximately linearly with increasing numbers of carbon atoms. This is true not only among the members of each series, but also between different series of compounds.[6,10,14,15,28,43,44] Even more significantly, the contribution of a polar- or hydrogen-bonding end group changes very little with the chain length — the effect of hydrogen bonding and polarity remains unchanged or undiluted by the increasing nonhydrogen bonding and nonpolar portions of the molecules.

Thus,

$$V = M\rho^{-1} = \sum_z {}^zV \tag{21}$$

where z represents the contributing group. (Group contributions are found to be preferable

TABLE 8
Atomic Attraction Constants at 25°C

Atom or structural feature, *z*	Bond type	${}^zF/J^{1/2}\ cm^{3/2}\ mol^{-1}$
C		0.0
H		140.1
O	Ether	256
O	Ester	256
O	Ketone	685
O	Primary alcohol	736
O	Secondary alcohol	614
O	Phenol	511
S	Thioether	460
S	Thiol	(511)
F		164
Cl		471
Br		614
I		859
Double bond (nonaromatic)		164
Double bond (aromatic)		272
Triple bond		440
N	Aliphatic primary amine	205
N	Aliphatic secondary amine	286
N	Aromatic primary amine	133
N	Heterocycle	235
N	Nitrile	982
N + O	Aliphatic nitro	941
N + O	Aromatic nitro	665
N + O	Acid amide,  $-\underset{\underset{\displaystyle O}{\|}}{C}-NH-$	1227
N + O	Acid amide,  $-\underset{\underset{\displaystyle O}{\|}}{C}-N$	818
Nonaromatic ring		123
Ramification in chain		−92
Conjugation of double bonds		51
2 OHs on adjacent Cs		−389

Adapted from van Krevelen, D. W., *Fuel*, 44, 229, 1965.

to "atom" contributions, which tend to be more dependent on the nature of the surrounding atoms.) For an homologous series the additive character can be tested by plotting ρ^{-1} against M^{-1}. If the increments for the repeating units (u) and for the constant "end" groups (e) of the molecule are designated ${}^uM$, ${}^uV$ and ${}^eM$, ${}^eV$, respectively, for the molar masses and molar volumes, it can be shown[45] that

$$\rho^{-1} = {}^uV/{}^uM + ({}^uM\,{}^eV - {}^eM\,{}^uV)M^{-1}/{}^uM \qquad (22)$$

so for exact additivity a set of lines is obtained, intersecting at (0, ${}^uV/{}^uM$). Exner[28] found that the additivity criterion was better fulfilled at constant temperature than at the individual boiling points.

The degree of molecular flexibility (conformational freedom) can influence the space requirement of groups.[46] Askadskii and co-workers[47-50] have discussed molar volumes in terms of the van der Waals volumes, ${}^zV_v$ of the constituent atoms or groups, and the molecular packing coefficient k which they defined

$$k = (N_A/V)\sum_z {}^zV_v = (N_A\rho/M)\sum_z {}^zV_v \tag{23}$$

where N_A is the Avogadro constant. Values of ${}^zV_v$ are given in Table 9; it should be noted that these are molecular constants, in units of Å^3, which must be multiplied by N_A to provide group molar constants. van der Waals volumes and molecular packing factors have been used widely in other ways related to cohesion parameters.[51-53]

Some group contributions to molar volumes at 25°C are included in Tables 2 and 3, and van Krevelen[15] has provided a summary of other values. This information may be used to estimate molar volumes for compounds when experimental values are unavailable, or to check that the additivity in a function of the form of Equation 7 is fulfilled with an accuracy greater than that of the molar volume alone.[28] Information on group molar volumes of polymers is included in Section 13.1, and the significance of molar volume in the activity of drugs in Chapter 19. For the "molar surface" modification of the Hildebrand-Scatchard equation,[54,55] molecular surface increments may be combined in the same way as volume increments.

6.6 GROUP COHESION PARAMETERS

During their search for improved methods of cohesion parameter calculations based on group contributions, Rheineck and Lin[14] plotted Hildebrand parameters against numbers of carbon atoms, *n*, in homologous series. For the hydrocarbons (Figure 2) a straight line relationship exists above about five carbon atoms; Hildebrand parameters have been evaluated[56] for *n*-alkanes up to C_{25}. For the other homologous series (Figure 3) no simple relationship is apparent.

In alternative methods of interpolating and extrapolating cohesion parameters, Rätzsch and Krahn[57] found that graphs of log δ against n^{-1} were linear, while Watanabe and Sugiyama[58] plotted log δ against log M to give straght lines for homologous series of saturated aliphatic hydrocarbons, alcohols, alkylbenzenes, ethers, ketones, and monobrominated hydrocarbons, but slightly curved lines for nitriles and esters of acetic acid.

Konstam and Feairheller[59] proposed a modified method for calculating Hildebrand parameters more directly from functional group contributions. In general, straight lines result when the Hildebrand parameters of a homologous series of monofunctional compounds are plotted against the reciprocal of the molar volume, V^{-1} (Figure 4):[59,60]

$$\delta = A + BV^{-1} \tag{24}$$

as discussed further in Section 10.1. This is equivalent to plotting $(-UV)^{1/2}$ against the number, *n*, of carbon atoms if V is a linear function of n and is more satisfactory for estimating the Hildebrand parameter of high molar mass members of a homologous series because the intercept of the line with the δ axis represents the Hildebrand parameter of an infinitely long member of the series ($V^{-1} = 0$). This means that all higher members of the series fall on a line between this axis and the first datum point and so can be readily obtained by extrapolation. (The lighter members of the homologous series of unsubstituted hydrocarbons are exceptional in not lying on a straight line when plotted against V^{-1}.) The functional group molar volumes may also be estimated from this information.

The analysis can be extended in terms of end groups (*e*) and repeating units (*u*).[61]

$$\delta = \sum_z {}^zF/V = [{}^uF(V - {}^eV)/{}^uV + {}^eF]/V \tag{25}$$

TABLE 9
van der Waals Volumes of Atoms and Atomic Groups

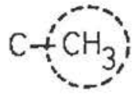
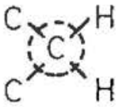
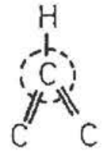
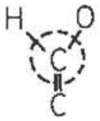
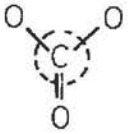
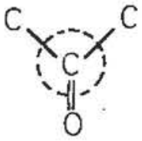
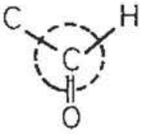
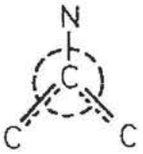
Atom or group	Bond lengths/Å	^aV_w/Å^3
	C–C, 1.48	22.7
	C–C, 1.54, 1.48	12.6
	C–C, 1.40	7.8
	C–C, 1.40; C–H, 1.08	13.9
	C–O, 1.50; C–H, 1.08; C=O, 1.34	16.2
	C–O, 1.37; C–H, 1.08	5.2
	C–O, 1.50; C=O, 1.28	19.0
	C–C, 1.54; C=O, 1.28	12.8
	C–C, 1.45; C–H, 1.08; C=O, 1.28	16.9
	C–C, 1.40; C–N, 1.37	10.2

TABLE 9 (continued)
van der Waals Volumes of Atoms and Atomic Groups

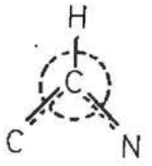
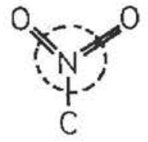
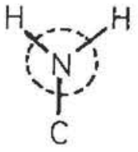
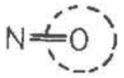
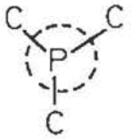
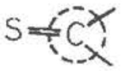
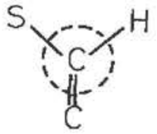
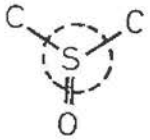
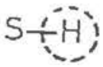
Atom or group	Bond lengths/Å	$^{z}V_{w}$/Å^3
	C–C, 1.40; C–H, 1.08; C–N, 1.34	14.8
	N–H, 1.08	3.5
	C–N, 1.37; N=O, 1.20	7.0
	C–N, 1.37; N–H, 1.08	8.7
	N=O, 1.20	7.2
	C–P, 1.81	14.7
	C=S, 1.71	20.2
	C–S, 1.76	16.5
	C=C, 1.34; C–S, 1.76, C–H, 1.08	14.2
	C–S, 1.76; S=O, 1.44	14.7
	C–S, 1.76; S–H, 1.33	19.5
	S–H, 1.33	3.2

TABLE 9 (continued)
van der Waals Volumes of Atoms and Atomic Groups

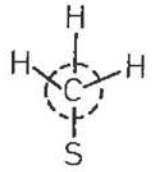
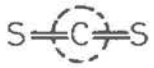
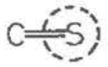
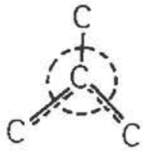
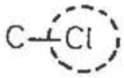
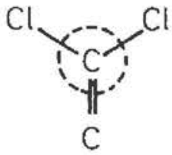
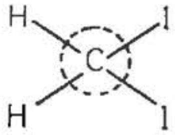
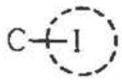
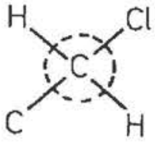
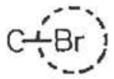
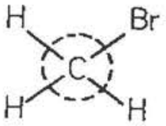
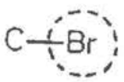
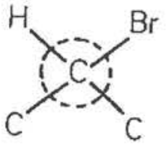
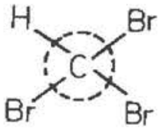
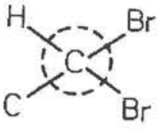
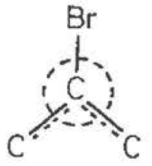
Atom or group	Bond lengths/Å	$^{a}V_w$/Å^3
	C–H, 1.08; C–S, 1.76	18.4
	C–S, 1.55	14.9
	C–S, 1.55	19.7
	C–C, 1.40; C–Cl, 1.70	10.5
	C–Cl, 1.70	19.5
	C=C, 1.34; C–Cl, 1.77	11.0
	C–H, 1.08; C–I, 2.21	13.5
	C–I, 2.21	38.4
	C–C, 1.54; C–H, 1.08: C–Cl, 1.77	14.1
	C–Br, 1.85	27.1
	C–H, 1.08; C–Br, 1.94	17.7
	C–Br, 1.94	27.3

TABLE 9 (continued)
van der Waals Volumes of Atoms and Atomic Groups

Atom or group	Bond lengths/Å	$^{z}V_{z}$/Å^3
	C–C, 1.54; C–H, 1.08; C–Br, 1.94	9.6
	C–H, 1.08; C–Br, 1.94	10.5
	C–C, 1.54; C–H, 1.08; C–Br, 1.94	10.0
	C–C, 1.40; C–Br, 1.85	9.9

Adapted from Askadskii, A. A., Kolmakova, L. K., Tager, A. A., Slonimskii, G. L., and Korshak, V. U., *Dokl. Akad. Nauk. SSSR*, 226, 857, 1976; *Dokl. Phys. Chem.*, 226, 99, 1976; *Vysokomol. Soedin. Ser. A* 19, 1004, 1977; *Polym. Sci. U.S.S.R.*, 19, 1159, 1977.

where $(V - {^eV})/{^uV}$ is a measure of the number of repeating units. Group Hildebrand parameters may be defined,

$$^{z}\delta = {^{z}F}/{^{z}V} \tag{26}$$

so

$$^{u}\delta = {^{u}F}/{^{u}V}, \qquad {^{e}\delta} = {^{e}F}/{^{e}V} \tag{27}$$

and

$$\delta = {^{u}\delta}(1 - {^{e}V}/V) + {^{e}\delta}{^{e}V}/V \tag{28}$$

which has the same form as Equation 24. The calculation of polymer cohesion parameters is discussed further in Section 14.8. Table 10 lists some group cohesion parameters and group molar volumes. The group molar volumes may be compared with the molar volumes of their molecular analogues, that is of molecules consisting of functional group plus hydrogen atom. For example, water ($V = 18.0$ cm^3 mol^{-1}) and acetic acid ($V = 57.9$ cm^3 mol^{-1}) have rather smaller molar volumes than –OH ($^{z}V = 19.7$ cm^3 mol^{-1}) and CH_3COO– ($^{z}V = 58.5$ cm^3 mol^{-1}) because of the extensive hydrogen bonding, but most molecules are slightly larger than the sum of the volumes of their functional groups.

The group molar attraction constants also calculated by Konstam and Feairheller[59] are listed in Table 11, along with Small's[32] earlier values. It should be noted that Small's value for the hydroxyl group represents only the cohesive pressure resulting from dispersion, while

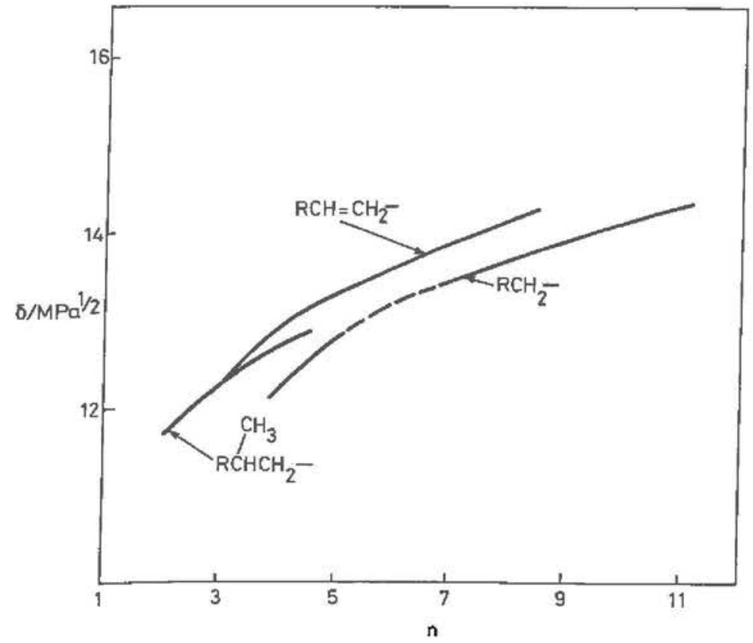


FIGURE 2. Hildebrand parameters of hydrocarbons as functions of numbers of carbon atoms. (Adapted from Rheineck, A. E. and Lin, K. F., *J. Paint Technol.*, 40, 611, 1968.)

the method of calculation of Konstam and Feairheller takes hydrogen bonding into account. (In fact,[62] Small's method provides a reasonable estimate of internal pressure rather than cohesive pressure: see Section 7.5.) Sears and Darby[102] applied Small's method to plasticizers, and many other estimates of Hildebrand parameters and related quantities have been based on these particular attraction constants, despite the publication of several revised sets (Section 6.4).

Askadskii and coworkers[47-50] calculated cohesion parameters by means of the van der Waals volumes described in the previous section. It follows from the definition of the packing coefficient *k* that

$$\delta^2 = -U/V = -\frac{Uk}{N_a\sum_z {}^{z}V_v} = \frac{U^*}{N_A\sum_z {}^{z}V_v} = -\frac{\sum_z {}^{z}U^*}{N_A\sum_z {}^{z}V_v} \qquad (29)$$

where $-U^*$ is the effective molar cohesive energy (the molar cohesive energy, $-U$, divided by the factor describing the number of times the van der Waals volume is smaller than the molar volume). The effective cohesive energy atomic contributions are listed in Table 12, and the denominator terms may be evaluated from the data in Table 9. These have been used both for liquids, and for polymers (Section 14.8).

Fisher[43,63] developed simple logarithmic equations for relating homolog cohesion parameters to number of carbon atoms (n) of the form $\delta = b + m \log (n + k)$. Cohesion parameters of some moderately polar homologs could be represented by simple linear equations, $\delta = b + m\,n$. The tables of b, m, and k values can be used to estimate Hildebrand parameters for a very large number of compounds. Also, the logarithm expression may be used to relate Hildebrand parameters to other quantities such as molar volume, boiling point, and vaporization enthalpy, which are linearly related to homolog chain length. Fisher has

ıccount.
ıer than
ɔ plasti-
ve been
sed sets

van der
ɔacking

(29)

ivided
an the
le 12,
: been

n pa-
esion
equa-
ɔrand
ıy be
ɔoint,
r has

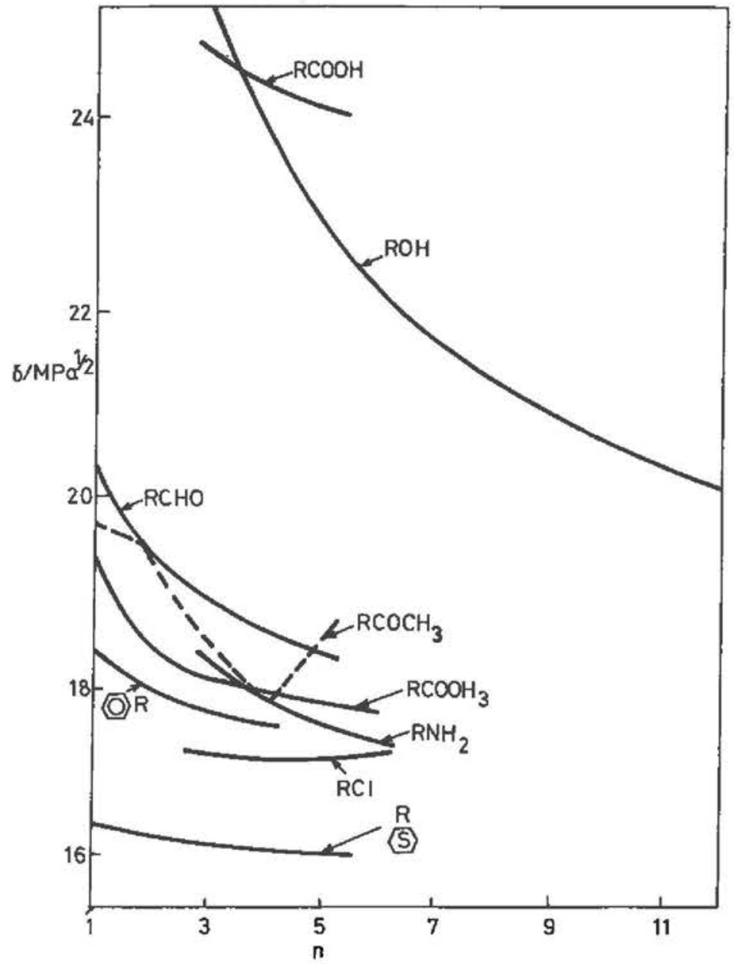


FIGURE 3. Hildebrand parameters of *n*-alkyl derivatives as functions of number of carbon atoms. (Adapted from Rheineck, A. E. and Lin, K. F., *J. Paint Technol.*, 40, 611, 1968.)

proceeded to devise alternative equations correlating Hildebrand parameters and other properties of homologs with chain length.[64,65]

A novel correlation[66] of cohesion energy parameters is based on the ratio of the sum of atomic weights of hetero atoms in the liquid molecule to the total molecular weight, and the ratio of the number of methyl or CF_3 groups per molecule to the total number of carbon atoms per molecule.

6.7 HOMOMORPHS AND DISPERSION COHESION PARAMETERS

In any multicomponent cohesion parameter system there arises the problem of evaluating the various components separately, and one obvious approach is to compare the properties of compounds which differ only in the presence or absence of a certain group. Here the homomorph concept is important:[67] the homomorph of a polar molecule is a nonpolar molecule having very nearly the same size and shape. Bondi and Simkin[68,69] proposed that for the purpose of estimating the dispersion component of cohesive pressure or cohesion

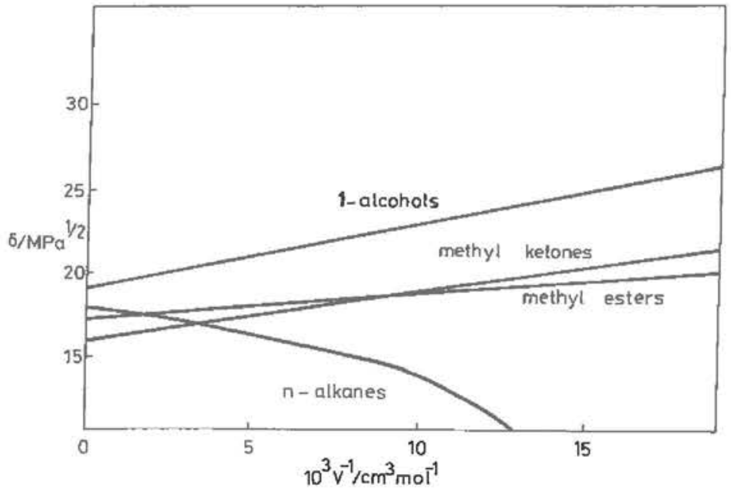


FIGURE 4. Hildebrand parameters of homologous series as functions of reciprocal molar volume. (Adapted from Konstam, A. H. and Feairheller, W. R., Jr., *Am. Inst. Chem. Eng. J.*, 16, 837, 1970.)

parameter, the homomorph of a polar molecule is that hydrocarbon whose structure is the same as that of the polar molecule, the vaporization enthalpy of the homomorph being evaluated at the same reduced temperature as that of the polar derivative. Following the additional recommendation[70,71] that the homomorph should have the same molar volume as well as a structure similar to that of the polar compound, Blanks and Prausnitz[72,73] published a homomorphic plot of the energy of vaporization for straightchain hydrocarbons (Figure 5). On the same basis, Weimer and Prausnitz[73] prepared homomorph plots of the cohesive pressure against molar volume at various reduced temperatures for alkanes, cycloalkanes, and aromatic hydrocarbons (Figures 6 to 8). (The axes in Figures 1 to 3 of Weimer and Prausnitz[74] should be labeled "cal cm^{-3}", and Equation 9 lacks the factor *RT* in the last two terms.[76]) The figures also have been reproduced elsewhere.[17,75] The cohesive pressure properties of a series of similar liquids vary in a smooth, continuous manner with their molar volumes, and Thompson[17,77] has expressed this analytically. Similar homomorphic plots have been presented by Helpinstill and Van Winkle.[78]

Wingefors and Liljenzin[79,80] developed a new homomorph equation for the calculation of dispersion cohesive pressure, based on Antoine constants and vaporization enthalpies at the boiling point and at 25°C. This correlation is depicted here for primary alcohols at 25°C (Figure 9a), *n*-alkanes at 25°C (Figure 9b), and *n*-alkanes at their normal boiling points (Figure 9c). The nonlinearity of the *V* scale should be noted; δ_λ^2 is a linear function of *V* raised to the power of θ:

$$\delta\lambda^2/\mathrm{J\ cm^{-3}} = (-U/V)/\mathrm{J\ cm^{-3}} = a(T_r) - b(T_r)V^\theta$$

where

$$\theta = 0.124687, \qquad (30)$$

$$a(T_r) = 1022.31 - 1586.36T_r + 1082.07T_r^2$$

$$b(T_r) = 277.790 - 531.335\,T_r + 482.039T_r^2$$

The broken lines in Figure 9 indicate a region where Equation 30 has limited accuracy.

Pussemier et al.[104] used the homomorph principle in evaluating Hildebrand parameters

TABLE 10
Group Cohesion Parameters and Group Molar Volumes of Some Functional Groups

Group, z	${}^{z}\delta$/MPa$^{1/2}$	${}^{z}V$/cm^3 mol^{-1}
$-NH_2$	24.03	29.49
–F	13.46	30.30
–Cl	18.18	34.98
–Br	19.33	33.07
–I	19.80	42.30
–COOH	29.60	36.28
–OH	41.50	19.66
–CHO	22.15	37.22
–(CO)–	28.47	32.52
CH_3CO–	23.13	53.49
–O–	20.54	27.96
–CN	30.40	31.23

Adapted from Konstam, A. H. and Feairheller, W. R., Jr., *Am. Inst. Chem. Eng. J.*, 16, 837, 1970.

for pesticides (containing highly polar bioactive functions) from experimental information on compounds corresponding to the aromatic portions of the pesticide molecules.

Varushchenko, Loseva, and Druzhinina[101] used the assumption[19] that a carbon-chlorine bond and three carbon-hydrogen bonds make almost equal contributions to the dispersion energy of a polar liquid to calculate

$$\Delta U^{\circ}_{p} = \Delta U^{\circ}(C_nH_{2n}Cl_2) - \Delta U^{\circ}(C_{n+2}H_{2n+6})$$

and so separated polar and dispersion components. Another experimental approach to information of this kind is gas-liquid chromatography (Section 18.3).

From graphs or functions such as those above, the dispersion cohesive pressure, $-U_d/V$, and dispersion parameter, δ_d, at any desired molar volume and temperature may be determined for a particular type of molecular skeleton. However, there are difficulties. Hansen and Beerbower[76] have pointed out that the homomorph charts of Weimer and Prausnitz[73] and of Helpinstill and Van Winkle[78], which were extended (but not used) by Beerbower and Dickey,[81] yield dispersion parameter values higher than those of Blanks and Prausnitz.[73] This last set was the basis for several subsequent successful correlations by Hansen,[82,83] Beerbower[81,84,85] and Zisman,[86] as well as the data used by Hansen and Beerbower.[76] When using group contribution and cohesion parameter data from different literature sources, it is essential to check that they are based on the same models and assumptions, and that they are self-consistent.

6.8 HANSEN PARAMETER GROUP CONTRIBUTIONS

It would be useful to be able to estimate the Hansen parameters δ_d, δ_p, and δ_h (Section 5.9) directly from molecular physical properties, but although correlations may be found between the cohesion parameter components and these quantities (Section 8.2, and in particular the work of Peiffer,[53] Loev and Lavrishchev,[87] Stekol'schchikov et al.,[88] and Martin, Wu, Adjei, and Beerbower[89,90]), it is usually more convenient to use methods based on structural combinations. If a quick estimate of the dispersion parameter is required, the dispersion contributions of Table 13 can be used:[15,76,91]

TABLE 11
Group Molar Attraction Constants at 25°C

		${}^zF/\mathrm{J}^{1/2}\ \mathrm{cm}^{3/2}\ \mathrm{mol}^{-1}$	
Group, *z*	**Bond type**	**Small[32]**	**Konstam and Feairheller[59]**
$-CH_3$		438	—
$-CH_2$	Single	272	—
>CH–	Single	57	—
>C<	Single	−190	—
$CH_2=$	Double	389	—
–CH=	Double	227	—
>C=	Double	39	—
CH≡C–	Triple	583	—
–C≡C–	Triple	454	—
Phenyl		1503	—
Phenylene (*o*,*m*,*p*)		1346	—
Naphthyl		2344	—
Ring, 5-membered		215-235	—
Ring, 6-membered		195-215	—
Conjugation		40-60	—
S	Sulfide	460	—
SH	Thiol	644	—
ONO_2	Nitrate	~900	—
NO_2	Aliphatic nitro	~900	—
PO_4	Organic phosphate	~1020	—
H	Variable	160-205	—
–CHO		—	824
–O–	Ether	143	575
–CO–	Ketone	563	681
–COO–	Ester	634	—
–COOH		—	1074
CN		839	948
Cl	Single	552	636
Cl	$>CCl_2$	532	636
Cl	$-CCl_3$	511	493[a]
Cl	>C(Cl)–C(Cl)<	—	497
Br	Single	696	736
Br	$>CBr_2$	—	677
Br	$-CBr_3$	—	581[a]
Br	>C(Br)–C(Br)<	—	630
F	Single	—	407
CF_2	*n*-Fluorocarbon	307	311
CF_3	*n*-Fluorocarbon	561	—
I	Single	869	839
OH	Single	348[b]	816[b]
OH	Diol	—	634
NH_2		—	710

[a] Values based on data for only one compound.
[b] See text for explanation of discrepancy between values of ${}^zF$ for –OH group.

$$\delta_d = \left(\sum_z {}^zF_d\right)/V \qquad (31)$$

If only one polar group is present, it is possible to evaluate δ_p from Table 7 by means of

$$\delta_p = F_p/V \qquad (32)$$

TABLE 12
Effective Cohesive Energy Atomic Contributions[47-50]

Atom or molecular feature, z	$-{}^{z}U^{*}$/kJ mol^{-1}
Carbon	2.304
Hydrogen	0.200
Oxygen	0.597
Nitrogen	5.04
Fluorine	0.101
Chlorine	−0.93
Bromine	2.44
Iodine	7.11
Sulfur	7.32
Dipole-dipole coupling in dipolar aprotic solvents	6.79
Dipole-dipole coupling in amide-type solvents	6.79
Dipole-dipole coupling in dimethylsulfoxide type solvents	10.88
Hydrogen bonding	16.44
Aromatic ring (skeleton)	2.98
Double bond	−1.35

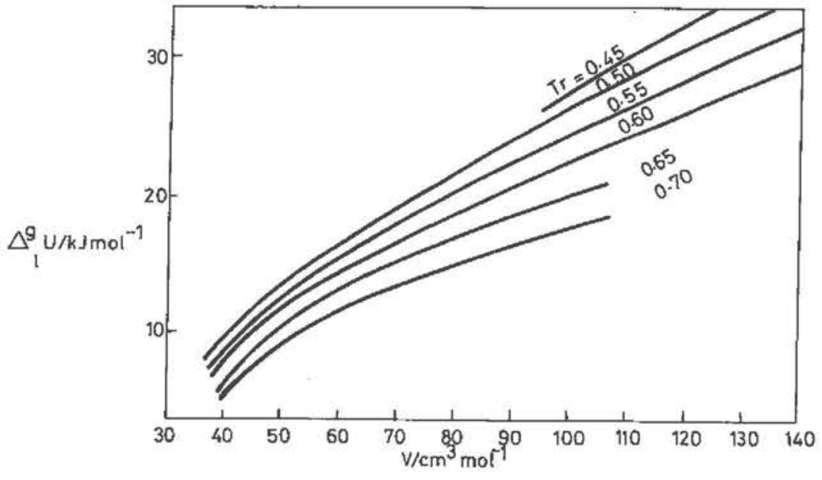


FIGURE 5. Vaporization energy for straight-chain hydrocarbons plotted against molar volume at various reduced temperatures. (Adapted from Blanks, R. F. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.*, 3, 1, 1964.)

but for more than one polar group it is necessary to correct for the interaction of polar groups by using[15]

$$\delta_p = \left(\sum_z {}^{z}F_p^2\right)^{1/2} / V \tag{33}$$

This must be reduced by multiplying δ_p calculated by Equation 33 by a symmetry factor if two identical polar groups are present in symmetrical positions:

- 0.5 for one plane of symmetry
- 0.25 for two planes of symmetry
- 0 for more planes of symmetry

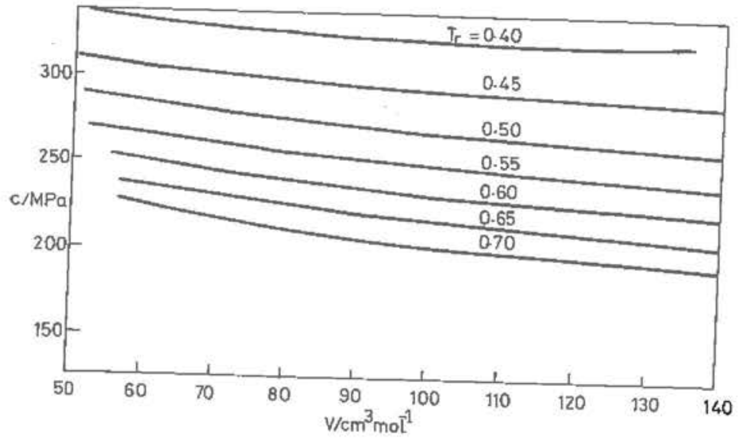


FIGURE 6. Homomorph plots for *n*-alkanes of cohesive pressure against molar volume at various reduced temperatures. (Adapted from Weimer, R. F. and Prausnitz, J. M., *Hydrocarbon Proc. Petr. Ref.*, 44, 237, 1965: see text.)

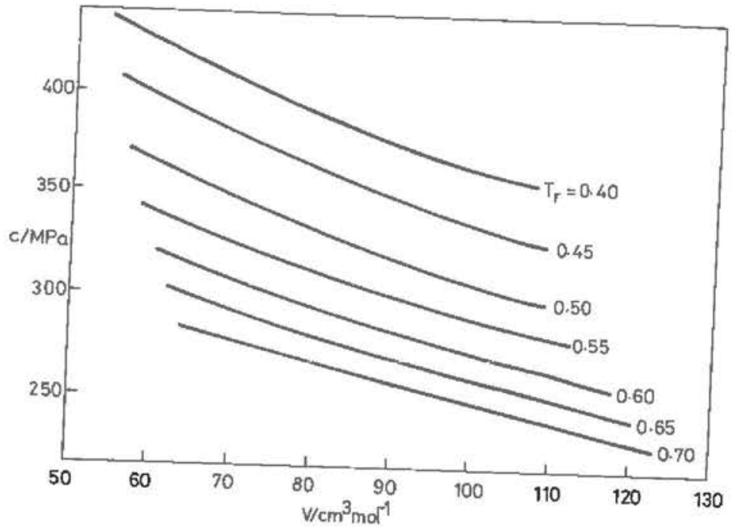


FIGURE 7. Homomorph plots for cycloalkanes of cohesive pressure against molar volume at various reduced temperatures. (Adapted from Weimer, R. F. and Prausnitz, J. M., *Hydrocarbon Proc. Petr. Ref.*, 44, 237, 1965: see text.)

These factors are included with the ^zF_p values in Table 13. Hansen and Beerbower[76] provided alternative values, warning against indiscriminate addition of functional group contributions and pointing out that the effect of adding a second chlorine could reduce δ_p, but ortho –COO– groups in phthalate could quadruple δ_p.

Hoy[35,36] used a group contribution method for the polar cohesion parameter (see Sections 5.11 and 6.4) based on

$$\delta_p = \delta_t\left(\sum_z {}^zF_p / \sum_z {}^zF\right) \qquad (34)$$

with the ^zF_p values in Table 7.

0

provided
tributions
out ortho

Sections

(34)

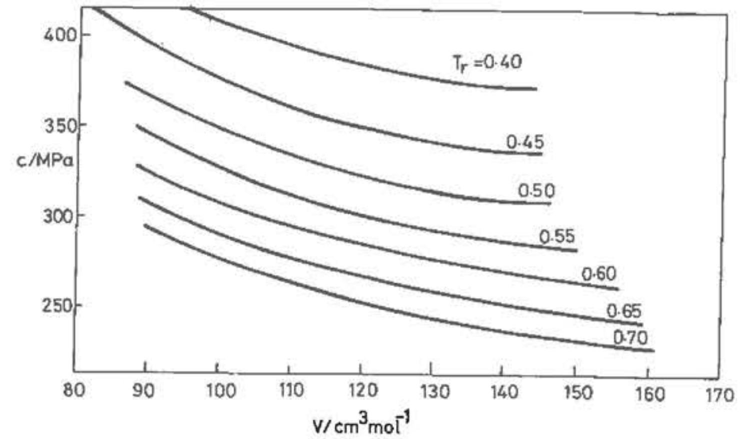


FIGURE 8. Homomorph plots for aromatic hydrocarbons of cohesive pressure against molar volume at various reduced temperatures. (Adapted from Weimer, R. F. and Prausnitz, J. M., *Hydrocarbon Proc. Petr. Ref.*, 44, 237, 1965: see text.)

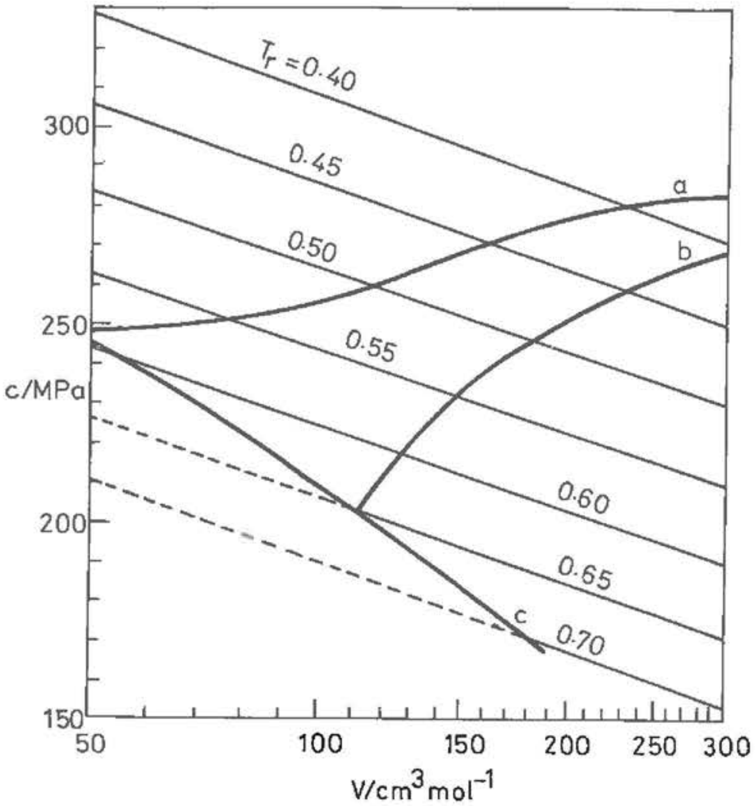
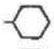
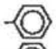
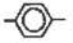


FIGURE 9. Cohesive pressures of *n*-alkanes in terms of molar volume and reduced temperature: a, primary alcohols; b, *n*-alkanes at 25°C; and c, *n*-alkanes at their normal boiling points. (Adapted from Wingefors, S. and Liljenzin, J. O., *J. Chem. Technol. Biotechnol.*, 31, 523, 1981.)

TABLE 13
Dispersion and Polar Group Molar Attraction Contributions

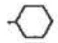
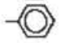
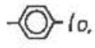
Structural group	${}^zF_d/J^{1/2}\ cm^{3/2}\ mol^{-1}$ Koenhen and Smolders[91]	${}^zF_d/J^{1/2}\ cm^{3/2}\ mol^{-1}$ van Krevelen[15]	${}^zF_p/J^{1/2}\ cm^{3/2}\ mol^{-1}$ van Krevelen[15]	$({}^zF_p = {}^zV\ {}^z\delta_p)/J^{1/2}\ cm^{3/2}\ mol^{-1}$ Hansen and Beerbower[76]
$-CH_3$	411	420	0	—
$-CH_2-$	284	270	0	—
$>C-$	104	80	0	—
$>C<$	—	−70	0	—
$=CH_2$	—	400	0	—
$=CH-$	—	200	0	—
$=C<$	—	70	0	—
	—	1620	0	—
	1640	—	—	—
	1510	1430	110	—
 (o, m, p)	1350	1270	110	—
$-F$	—	(220)	—	460 ± 50
$-Cl$	—	450	550	610 ± 200
$>Cl_2$	—	—	—	360 ± 50
$-Br$	—	(550)	—	610 ± 50
$-I$	—	—	—	665 ± 50
$-CN$	446	430	1100	1070 ± 100
$-OH$	202	210	500	510 ± 60
$(-OH)_n$	—	—	—	n(350 ± 50)
$-O-$	—	100	400	410 ± 100
$-COH$	—	470	800	—
$-C{=}O$	325	—	—	—
$-CO-$	—	290	770	800 ± 30
$-COOH$	409	530	420	450 ± 20
$-COO-$	395	390	490	510 ± 50
$HCOO-$	—	530	—	—
$-NH_2$	—	280	—	610 ± 200
$-NH-$	143	160	210	205 ± 30
$-N<$	—	20	800	—
$-NO_2$	440	500	1070	1020 ± 100
$-S-$	—	440	—	—
$=PO_4^-$	—	740	1890	—
Ring	—	190	—	—
One plane of symmetry	—	—	0.50 ×	—
Two planes of symmetry	—	—	0.25 ×	—
More planes of symmetry	—	—	0 ×	—

Although the *F*-method is not applicable directly to the calculation of δ_h, Hansen and Beerbower[76] have assumed that hydrogen bonding cohesive energy is additive, leading to

$$\delta_h = \left(\sum_z - {}^zU_h/V\right)^{1/2} \tag{35}$$

Two sets of estimates of $-{}^zU_h$ are shown in Table 14. Again, extreme caution is needed in adding group contributions in the use of a single hydrogen bonding parameter to describe

TABLE 14
Hydrogen Bonding Parameter Group Contributions

Structural group, z	${}^{z}U_h$/J mol^{-1} van Krevelen[15]	$-{}^{z}U_h = {}^{z}V\,{}^{z}\delta_h^2$/J mol^{-1} Hansen and Beerbower[76] Aliphatic	Aromatic
–CH_3	0	—	—
–CH_2–	0	—	—
>CH–	0	—	—
>C<	0	—	—
=CH_2	0	—	—
=CH–	0	—	—
=C<	0	—	—
	0	—	—
	0	—	—
 (o, m, p)	0	—	—
–F	—	~0	~0
–Cl	400	400 ± 80	400 ± 80
>Cl_2	—	690 ± 40	750 ± 40
–Br	—	2100 ± 400	2100 ± 400
–I	—	4000 ± 800	—
–CN	2500	2100 ± 800	2300 ± 800
–OH	20000	19500 ± 1700	19500 ± 2100
–$(OH)_n$	—	n(19500 ± 1700)	n(19500 ± 1700)
–O–	3000	4800 ± 1200	5200 ± 1200
–COH	4500	—	—
–CO–	2000	3300 ± 600	3300 ± 600
–COOH	10000	11500 ± 1000	9400 ± 1000
–COO–	7000	5200 ± 600	3300 ± 600
–NH_2	8400	5600 ± 800[a]	9400 ± 800[a]
–NH–	3100	3100 ± 800	—
–N<	5000	—	—
–NO_2	1500	1700 ± 200	1700 ± 200
=PO_4^-	13000	—	—

[a] Data from Bondi[8] corrected to 25°C and $V\delta_p^2$ subtracted. For important steric shielding effects, see his Tables 7.6 and 7.7.

an interaction really requiring both donor and acceptor components (Section 5.5), where "chameleonic" effects can occur.

Meusberger[92] presented the Hansen parameter group contributions in Table 15 compiled by Beerbower as a compromise between the 1971 Hansen-Beerbower data (Table 11, Chapter 5) and Hoy's cohesion parameters (Table 18, Chapter 5), and which at least have the advantage of being the most recently compiled comprehensive set. Examples of calculations of component cohesion parameters are provided in Table 16.

6.9 PARTICIPATING AND NONPARTICIPATING GROUPS

In applying cohesion parameter methods to the solubility of steroids and other drugs, Ostrenga and Steinmetz[34,93,94] formulated a parameter which assessed the fraction of the liquid molecule which could participate in specific interactions, considered to be highly significant in the solubilization process:

TABLE 15
Group Contributions for Molar Volumes and Hansen Parameters Compiled by Beerbower

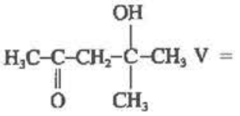
Structural group	M g mol^{-1}	${}^zV$ cm^3 mol^{-1}	${}^zF_d$ $(= {}^zV\,{}^z\delta_d)$ J$^{1/2}$ cm$^{3/2}$ mol^{-1}	${}^zF_p$ $(= {}^zV\,{}^z\delta_p)$ J$^{1/2}$ cm$^{3/2}$ mol^{-1}	${}^zV\,{}^z\delta_h^2$ J mol^{-1}
–CH$_3$	15.04	31.7	419	0	0
–CH$_2$–	14.03	16.6	270	0	0
>CH–	13.02	−1.0	80	0	0
>C<	12.01	−19.2	−70	0	0
=CH$_2$	14.03	32.1	403	94	143
=CH–	13.02	12.4	223	70	143
=C<	12.01	−5.7	45	70	143
5 or 6 member ring	0.00	13.5	190	0	0
Conjugation:chain	0.00	−1.7	0	0	563
Cis configuration	0.00	0.0	−409	0	0
Conjugation:ring	0.00	0.80	43	0	−227
–O–	16.0	3.80	100	401	1467
>C=O	28.0	10.5	291	769	978
–OCO–	44.0	18.96	391	489	3420
>PO$_4^-$	96.0	28.00	741	1000	6353
–CN	26.0	22.40	430	1101	1221
–NO$_2$	46.0	24.00	499	1070	732
–NH$_2$	16.0	17.93	370	419	3220
–NH–	15.0	4.50	160	211	1516
>N–	14.0	−9.00	31	149	366
–N=	14.0	4.00	164	1323	1759
–CONH	43.0	16.80	516	1270	5985
–CON<	42.0	13.20	301	1229	4772
–OH	17.0	10.47	211	499	9773
–COOH	45.0	27.83	530	419	4887
>SiO<	44.1	3.80	266	307	921
–Cl	35.5	25.30	419	614	205
–Cl aromatic	35.5	24.00	329	550	78
(–Cl)$_2$ adjacent	70.9	51.20	900	1101	880
>C=O	28.0	10.00	291	769	978
–F	19.0	18.00	221	542	0
–Br	79.9	29.00	1080	614	1023
–Br aromatic	79.9	30.00	550	401	440
(–Br)$_2$adjacent	159.8	54.00	1101	929	3224
–I	126.9	32.20	655	665	2046
–COO– ester	44.0	8.20	667	511	2557
–COO– ester aromatic	44.0	8.20	667	511	1636
–O–	16.0	3.60	235	409	2352
–O– aromatic	16.0	3.80	100	401	1467
–NH$_2$ amide	15.0	25.10	669	1023	5523
–S–	32.1	8.00	454	362	221
Phenyl–	77.1	75.40	1499	121	205
Phenyl<	76.1	60.40	1319	133	205
–NO$_2$ aromatic	46.0	24.00	499	1070	732
–NH– aromatic	15.0	4.50	160	211	1516
>N–aromatic	14.0	−9.00	31	149	366
>CO$_3$	60.0	22.00	640	221	2246
>CO$_3$ ring	60.0	22.00	761	1528	945
HCOO– formate	44.0	32.50	542	248	3226
–CO–O–CO– anhydride	72.0	30.00	675	1105	4838

Adapted from Meusberger, K. E., *Am. Chem. Soc. Symp. Ser.*, 371 (*Pesticide Formulations*), 151, 1988.

$^zV\,^z\delta_h^2$
J mol^{-1}

0
0
0
0
143
143
143
0
563
0
−227
1467
978
3420
6353
1221
732
3220
1516
366
1759
5985
4772
9773
4887
921
205
78
880
978
0
1023
440
3224
2046
2557
1636
2352
1467
5523
221
205
205
732
1516
366
246
945
226
838

TABLE 16
Group Molar Hansen Parameter Calculations for Diacetone Alcohol at 25°C



$H_3C-C(=O)-CH_2-C(OH)(CH_3)-CH_3$ V = 123.8 cm³ mol⁻¹

Group, z	$\sum_z {}^zF_d$/J$^{1/2}$ cm$^{3/2}$ mol^{-1} (Table 13)	$\sum_z {}^zF_p{}^2$/kJ cm^3 mol^{-2} (Table 13)	$-\sum_z {}^zU_h$/kJ mol^{-1} (Table 14)
3(–CH$_3$)	1260	0.0	0.0
(–CH$_2$)	270	0.0	0.0
(>C<)	−70	0.0	0.0
(–CO–)	290	593.0	2.0
(–OH)	210	250.0	20.0
	1960	843.0	22.0

δ_d = 1960/123.8 = 15.8 MPa$^{1/2}$ (Equation 31)

δ_p = 843.000$^{1/2}$/123.8 = 7.4 MPa$^{1/2}$ (Equation 33)

δ_h = (22.000/123.8)$^{1/2}$ = 13.3 MPa$^{1/2}$ (Equation 34)

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} = 21.9 \text{ MPa}^{1/2}$$

Adapted from van Krevelen, D. W., *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, 1976.

$$\delta = \delta_{sp} + \delta_{np} = (F_{sp} + F_{np})/V \tag{36}$$

$$\delta_{sp} = F_{sp}/V;\ \delta_{np} = F_{np}/V \tag{37}$$

$$f_{sp} = \delta_{sp}/\delta = F_{sp}/F = \sum_z {}^zF_{sp}/(\delta V) \tag{38}$$

The partial cohesion parameters, indicated here by δ_{sp} and δ_{np}, are the contributions made to δ by participating and nonparticipating functional groups, respectively. They are defined in terms of the corresponding molar attraction constants, F_{sp} and F_{np}, and the fractional participating molar attraction constant or fractional cohesion parameter is given by f_{sp}. F_{sp} values were calculated from Small's[32] group ^zF values, while δV values were obtained from whole-molecule sources if available, rather than by summing group contributions. For diols such as ethylene glycol and propylene glycol, the value of ^zF for a single –OH group was calculated from δV for the whole molecule less the $\epsilon_Z\,{}^zF$ value of the remaining groups. For strictly nonpolar (non-participating) liquids such as heptane, $f_{sp} = 0$, while for strictly polar or completely participating liquids such as water, $f_{sp} = 1$. The values for some other liquids are included in Table 17, rounded to two significant figures. This topic is referred to again in Section 19.1.

6.10 COMPARISON OF METHODS

The values reported by different authors of particular group contributions show considerable variation.[60,95-98] In particular, Jayasri and Yaseen[60,97] compared Hildebrand parameter values calculated by several group contribution methods with those reported on the basis of experimental data. They also reported (Table 18) preferred values, obtained after making linear plots of δ as functions of inverse molar volume (Sections 6.6 and 9.2).

TABLE 17
Participating Fractional Parameters

Liquid	f_{sp}
Water	1.00
Propylene glycol	0.60
Diethylene glycol	0.54
1,4-Butanediol	0.51
Glyceryol triacetate	0.50
Ethylene glycol diacetate	0.47
Propylene carbonate	0.46
Methyl Cellosolve®	0.45
Ucar® solvent LM	0.42
Cellosolve®	0.39
Carbitol®	0.36
Ethyl acetate	0.36
Methyl Cellosolve® acetate	0.35
Poly(ethylene glycol) 400	0.33
Cellosolve® acetate	0.32
Carbitol® acetate	0.29
Butyl Carbitol®	0.29
Pentyl acetate	0.24
Isopropyl myristate	0.11
Heptane	0.00

Adapted from Ostrenga, J. A. and Steinmetz, C., *J. Pharm. Sci.*, 59, 414, 1970.

TABLE 18
Hildebrand Parameter Values at 25°C Suggested by Jayasri and Yaseen[60,97] After Correlation With Inverse Molar Volume Dependence.

		δ/MPa$^{1/2}$			
Liquid	V cm^3 mol^{-1}	Jayasri & Yaseen	Hoy	Burrell	Hansen
	Alcohols				
Methanol	40.4	30.7	29.7	29.7	29.2
Ethanol	58.4	26.5	26.1	26.0	26.4
1-Propanol	74.7	24.7	24.9	24.3	24.5
1-Butanol	91.7	23.5	23.7	23.3	23.1
1-Pentanol, amyl alcohol	108.2	22.4	22.8	22.3	21.7
1-Hexanol	124.8	22.1	22.0	21.9	21.9
1-Heptanol	141.9	21.5	21.5	21.7	21.1
1-Octanol	157.9	21.1	21.1	21.1	19.8
1-Nonanol	174.3	20.7	20.7	—	—
1-Decanol	190.9	20.7	20.5	—	—
2-Propanol, isopropanol	60.1	23.7	23.4	23.5	23.6
Isobutanol, 2-methyl-1-propanol	74.1	23.0	23.0	—	22.8
2-Butanol, *sec* Butanol	74.1	22.8	22.7	22.1	22.2
2-Ethylbutanol	102.2	21.7	21.2	21.5	21.2
2-Ethylhexanol	130.2	20.7	20.8	—	20.2
Allyl alcohol, 2-propen-1-ol	58.2	25.5	25.7	—	24.9
	Aliphatic Hydrocarbons				
Methane	38.7	9.5	—	—	9.6
Ethane	53.6	11.6	—	—	11.6

TABLE 18 (continued)
Hildebrand Parameter Values at 25°C Suggested by Jayasri and Yaseen[60,97] After Correlation With Inverse Molar Volume Dependence.

Liquid	V cm^3 mol^{-1}	δ/MPa$^{1/2}$			
		Jayasri & Yaseen	Hoy	Burrell	Hansen
Propane	75.3	13.2	11.8	—	12.7
Butane	96.9	14.1	13.5	—	13.5
Pentane	115.3	14.5	14.4	14.3	14.4
Hexane	130.5	14.8	14.8	—	14.8
Heptane	146.5	15.1	15.3	15.1	15.2
Octane	162.3	15.3	15.4	15.6	15.4
Nonane	178.8	15.5	15.6	—	15.6
Decane	194.9	15.6	15.8	—	15.8
Cyclopentane	93.4	16.3	16.6	—	15.8
Cyclohexane	108.0	16.8	16.8	16.8	16.7
Aromatic Hydrocarbons					
Benzene	88.9	18.7	18.7	18.8	18.7
Toluene, methylbenzene	106.3	18.3	18.3	18.2	18.2
o-Xylene, 1,2-dimethylbenzene	120.6	18.1	18.5	18.4	18.4
m-Xylene, 1,3-dimethylbenzene	122.9	18.3	18.2	18.0	18.0
p-Xylene, 1,4-dimethylbenzene	123.3	18.0	18.1	17.9	17.9
Ethylbenzene	122.5	18.0	18.1	18.0	18.0
Propylbenzene	129.4	17.6	—	17.7	17.7
Isopropylbenzene	139.5	17.9	17.6	17.4	17.4
Styrene, ethenylbenzene	114.8	18.3	19.1	19.0	19.0
Esters					
Methyl formate	62.1	20.1	20.3	20.9	20.6
Ethyl formate	80.2	18.9	19.0	19.2	19.5
Propyl formate	97.8	18.3	—	18.8	19.6
Isobutyl formate	116.7	17.3	—	—	17.6
Isoamyl formate	133.4	17.1	—	—	17.3
Methyl acetate	79.9	19.1	19.4	19.6	19.4
Ethyl acetate	97.8	18.1	18.2	18.6	18.6
Propyl acetate	115.1	17.6	18.0	18.0	17.9
Butyl acetate	131.7	17.4	17.8	17.4	17.3
Isopropyl acetate	116.5	17.1	17.6	17.2	17.3
Isobutyl acetate	133.3	16.9	17.2	17.0	17.2
Isoamyl acetate	148.1	16.9	—	—	17.0
Methyl propionate	96.3	18.3	18.7	—	18.5
Ethyl propionate	114.0	17.6	17.9	—	17.9
Propyl propionate	131.6	17.3	—	17.4	16.9
Isobutyl propionate	146.7	16.5	—	—	16.5
Isoamyl propionate	165.8	16.7	—	—	16.7
Methyl butyrate	113.7	17.8	—	18.2	18.2
Ethyl butyrate	132.2	17.2	17.0	17.4	17.4
Propyl butyrate	148.1	17.1	—	17.2	16.9
Methyl isobutyrate	114.6	17.1	—	—	17.4
Ethyl isobutyrate	133.6	16.7	—	—	16.8
Propyl isobutyrate	147.3	16.7	—	—	16.3

TABLE 18 (continued)
Hildebrand Parameter Values at 25°C Suggested by Jayasri and Yaseen[60,97] After Correlation With Inverse Molar Volume Dependence.

Liquid	V cm^3 mol^{-1}	δ/MPa$^{1/2}$ Jayasri & Yaseen	Hoy	Burrell	Hansen
Ketones					
Acetone, 2-propanone	73.3	19.8	19.7	20.5	20.0
Methyl ethyl ketone, 2-butanone	89.6	18.9	19.3	—	19.0
Diethyl ketone, 3-pentanone	105.6	18.4	—	18.0	18.1
Methyl propyl ketone, 2-pentanone	106.1	18.3	—	17.8	18.3
Methyl butyl ketone, 2-hexanone	120.7	18.3	—	—	17.6
Methyl isobutyl ketone	124.9	18.1	—	17.2	17.5
Methyl amyl ketone	138.9	17.7	—	17.4	18.1
Ethyl butyl ketone	139.5	17.8	—	—	18.5
Dipropyl ketone	139.7	17.6	—	—	18.1
Methyl hexyl ketone	196.7	17.7	—	17.2	17.4
Cyclopentanone	88.7	20.6	21.5	21.3	21.6
Cyclohexanone	103.6	20.8	21.3	20.3	20.2
Acetophenone	117.1	21.5	21.6	—	19.8
Isophorone	150.5	19.2	19.2	18.6	19.9
Ethers					
Methyl isopropyl ether	100.9	15.7	—	—	15.4
Diethyl ether	103.9	15.2	15.4	—	15.6
Ethyl propyl ether	120.4	15.7	—	—	15.9
Ethyl butyl ether	136.6	15.9	15.7	—	16.5
Diisopropyl ether	142.1	14.9	14.4	—	14.4
Dibutyl ether	170.2	16.3	15.9	—	15.9
Carbitols®					
Methyl Carbitol	118.2	21.7	22.8	—	21.9
Carbitol	136.2	21.1	21.1	19.6	22.5
Butyl Carbitol	170.5	19.4	20.0	18.2	18.3
Diethyl Carbitol	182.0	17.1	17.1	—	18.4
Dibutyl Carbitol	248.0	16.8	17.0	—	17.7
Cellosolves®					
Methyl Cellosolve	79.1	23.3	23.9	22.1	24.7
Butyl Cellosolve	131.6	19.6	20.2	18.2	21.0
Diethyl Cellosolve	133.7	18.7	17.1	—	20.4
Dibutyl Cellosolve	209.0	16.4	16.8	—	17.1
Halogen Compounds					
Chloromethane, methyl chloride	57.5	16.4	—	—	—
Chloroethane, ethyl chloride	73.6	16.6	—	—	—
1-Chloropropane, propyl chloride	88.3	16.9	17.2	17.4	17.4
1-Chlorobutane, butyl chloride	104.7	16.9	17.1	—	17.3
2-Chloropropane, isopropyl chloride	90.0	16.4	16.5	—	16.5
2-Chlorobutane, *sec*-butyl chloride	106.1	16.6	16.6	16.6	16.6
2-Ethylhexylchloride	169.1	16.9	16.6	—	17.2
Chlorobenzene	101.7	19.8	19.8	19.4	19.6
Bromobenzene	104.7	20.6	20.2	—	20.0
o-Dichlorobenzene	112.7	21.1	20.5	20.5	20.4

een[60,97] After

urrell	Hansen
20.5	20.0
—	19.0
18.0	18.1
17.8	18.3
—	17.6
17.2	17.5
17.4	18.1
—	18.5
—	18.1
7.2	17.4
1.3	21.6
0.3	20.2
—	19.8
8.6	19.9
—	15.4
—	15.6
—	15.9
—	16.5
—	14.4
—	15.9
	21.9
5	22.5
2	18.3
	18.4
	17.7
	24.7
	21.0
	20.4
	17.1
	—
	—
	17.4
	17.3
	16.5
	16.6
	17.2
	19.6
	20.0
	20.4

TABLE 18 (continued)
Hildebrand Parameter Values at 25°C Suggested by Jayasri and Yaseen[60,97] After Correlation With Inverse Molar Volume Dependence.

Liquid	V cm^3 mol^{-1}	δ/MPa$^{1/2}$ Jayasri & Yaseen	Hoy	Burrell	Hansen
Tetrachloromethane, carbon tetrachloride	96.5	18.5	17.5	17.6	17.7
Trichloromethane, chloroform	79.7	18.6	18.7	19.0	18.8
1,2-Dichloroethane, ethylene dichloride	79.0	19.2	20.2	20.1	19.0
Trichloroethylene	90.3	18.9	18.7	19.0	19.0
1,3-Dichloropropane, propylene dichloride	97.5	18.8	18.5	19.3	19.3
1,1-Dichloroethane	84.3	19.0	18.3	—	20.0
	Amines				
Propylamine, propanamine	82.2	18.0	18.1	—	18.4
Butylamine, butanamine	98.8	17.6	17.7	—	—
Diethylamine	102.9	17.0	16.5	—	16.3
Hexylamine, hexanamine	132.7	17.3	17.3	—	—
Dipropylamine	137.0	16.2	16.3	—	15.9
Dibutylamine	168.5	16.4	16.7	—	16.7
	Anilines				
Aniline	91.1	21.3	21.9	—	22.6
Methyl aniline	108.7	20.3	20.1	—	21.4
Ethyl aniline	126.8	20.0	21.5	—	—
Dimethyl aniline	126.8	18.2	18.2	—	19.5
Butyl aniline	161.4	19.7	20.4	—	—
	Nitriles				
Acetonitrile	52.4	24.5	26.0	24.3	24.0
Propionitrile	70.3	21.9	22.0	22.1	21.5
Butyronitrile	86.8	20.9	20.8	21.5	20.4
Capronitrile, hexanenitrile	120.1	19.7	—	19.2	18.5

Not unexpectedly, comparison of calculated results with experiment for both liquids and polymers (Section 14.8) suggests that more recent sets of group contribution constants are preferable to Small's original values. However, despite the differences between the values in various sets of group constants, the molar cohesive energies and cohesion parameters for molecules obtained by adding the group contributions usually do not differ too widely, and each system usually provides values acceptable for many practical purposes. It is, of course, important to use self-consistent sets of group contributions. When different techniques are combined (e.g., δ_h contributions added to δ_d evaluated from molar attraction constants[103]) greater variations occur.

Like most other aspects of the cohesion parameter method, even the decision as to the preferred method of defining group contributions or of estimating values is often based on empirical observation. It is essential to be alert for any characteristics of a particular material or combination of materials that are not accounted for in the rather simple models which form the bases of the calculations.

The various cohesion parameter methods described in Chapters 5, 7, and 8 require specific data for each compound, but group methods can predict activity coefficients and other properties in systems containing previously unstudied compounds. Although the cohesion parameter group methods described in this chapter may be used for this purpose, the most popular approach is the UNIFAC (*UNI*QUAC *f*unctional group *ac*tivity) functional group method[99] based on the UNIQUAC (*uni*versal *qu*asi *c*hemical) equation.[100] Some comparisons are referred to in Section 7.8.

REFERENCES

1. **Yalkowsky, S. H., Flynn, G. L., and Slunick, T. G.,** Importance of chain length on physicochemical and crystalline properties of organic homologs, *J. Pharm. Sci.*, 61, 852, 1972.
2. **Leshchev, S. M., Starobinets, G. L., Rakhmanko, E. M., and Bubel, O. N.,** Influence of the solvent nature on the solvophobic effect, *Dokl. Akad. Nauk B.S.S.R.*, 31, 725, 1987.
3. **Munafo, A., Buchmann, M., Hô Nam-Tran, and Kesselring, U. W.,** Determination of the total and partial cohesion parameters of lipophilic liquids by gas-liquid chromatography and from molecular properties, *J. Pharm. Sci.*, 77, 169, 1988.
4. **Dunkel, M.,** Calculation of intermolecular forces in organic compounds, *Z. Phys. Chem.*, A138, 42, 1928.
5. **Hayes, R. A.,** The relationship between glass temperature, molar cohesion, and polymer structure, *J. Appl. Polym. Sci.*, 5, 318, 1961.
6. **Fedors, R. F.,** A method for estimating both the solubility parameters and molar volumes of liquids, *Jet Propul. Lab. Quart. Tech. Rev.*, 3(1), 45, 1973; *Polym. Eng. Sci.*, 14, 147, and 472, 1974.
7. **Bondi, A.,** On the solubility of paraffin-chain compounds, *J. Phys. Chem.*, 51, 891, 1947.
8. **Bondi, A. A.,** *Physical Properties of Molecular Crystals, Liquids and Glasses,* John Wiley & Sons, New York, 1968.
9. **Stein, S. E.,** Application of additive estimation methods to vaporization properties of liquids: n-alkanes, *J. Chem. Soc. Faraday Trans. I*, 77, 1457, 1981.
10. **Bunn, C. W.,** The melting points of chain polymers, *J. Polym. Sci.*, 16, 323, 1955.
11. **DiBenedetto, A. T.,** Molecular properties of amorphous high polymers. I. A cell theory for amorphous high polymers, *J. Polym. Sci., A-1*, 3459, 1963.
12. **Maffiolo, G., Vidal, J., and Renon, H.,** Cohesive energy of liquid hydrocarbons, *Ind. Eng. Chem. Fundam.*, 11, 100, 1972.
13. **van Krevelen, D. W. and Hoftyzer, P. J.,** Practical evaluation of the $[\eta]$-M relation, *J. Appl. Polym. Sci.*, 11, 2189, 1967.
14. **Rheineck, A. E. and Lin, K. F.,** Solubility parameter calculations based on group contributions, *J. Paint Technol.*, 40, 611, 1968.
15. **van Krevelen, D. W.,** *Properties of Polymers: Their Estimation and Correlation with Chemical Structure,* 2nd ed., Elsevier, Amsterdam, 1976.
16. **Kreibich, U. T. and Batzer, H.,** Influence of the segment structure and cross-linking on the glass transition T_g. Possibilities of predicting T_g using the values of cohesive energy E_{coh}, *Angew. Makromol. Chem.*, 83, 57, 1979.
17. **Kumar, R. and Prausnitz, J. M.,** Solvents in chemical technology, in *Solutions and Solubilities, Part I,* Dack, M. R. J., Ed., John Wiley & Sons-Interscience, New York, 1975, chap. 5.
18. **Meyer, E. F. and Wagner, R. E.,** Cohesive energies in polar organic liquids, *J. Phys. Chem.*, 70, 3162, 1966.
19. **Meyer, E. F., Renner, T. A., and Stec, K. S.,** Cohesive energies in polar organic liquids. 2. The *n*-alkyl nitriles and the 1-chloro-alkanes, *J. Phys. Chem.*, 75, 642, 1971.
20. **Meyer, E. F. and Hotz, C. A.,** Cohesive energies in polar organic liquids. 3. Cyclic ketones, *J. Chem. Eng. Data*, 21, 274, 1976.
21. **Meyer, E. F., Awe, M. J., and Wagner, R. E.,** Cohesive energies in polar organic liquids. 4. *n*-Alkyl acetates, *J. Chem. Eng. Data*, 25, 371, 1980.
22. **Lawson, D. D.,** Methods of calculating engineering parameters for gas separations, *Appl. Energ.*, 6, 241, 1980.
23. **Polak, J.,** Heat of vaporization and cohesion energy of liquids, *Collect. Czech. Chem. Commun.*, 31, 1483, 1966.
24. **Fried, V. and Schneier, G. B.,** Some comments on cohesion energies of liquids, *J. Phys. Chem.*, 72, 4688, 1968.
25. **Figgins, C. E., Risby, T. H., and Jurs, P. C.,** The use of partial molal entropies and free energies in the characterization of gas chromatographic stationary phases, *J. Chromatogr. Sci.*, 14, 453, 1976.

26. **Figgins, C. E., Reinhold, B. L., and Risby, T. H.,** Partial molal and mole fraction free energies as characterizers for stationary liquid phases, *J. Chromatogr. Sci.*, 15, 208, 1977.
27. **Risby, T. H., Jurs, P. C., and Reinhold, B. L.,** Use of thermodynamic solubility parameters for the characterization of liquid phases, *J. Chromatogr.*, 99, 173, 1974.
28. **Exner, O.,** Additive physical properties. II. Molar volume as an additive property, *Collect. Czech. Chem., Commun.*, 32, 1, 1967.
29. **Bowden, S. T. and Jones, W. J.,** Latent heat of vaporization and composition, *Philos. Mag.*, 39, 155, 1948.
30. **Wright, F. J.,** Latent heat of vaporization and composition, *Recl. Trav. Chim. Pays-Bas*, 79, 784, 1960.
31. **Scatchard, G.,** Equilibria in non-electrolyte solutions in relation to the vapor pressures and densities of the components, *Chem. Rev.*, 8, 321, 1931.
32. **Small, P. A.,** Some factors affecting the solubility of polymers, *J. Appl. Chem.*, 3, 71, 1953.
33. **Cammarata, A. and Yau, S. J.,** Molecular estimates for molar attraction constants, *J. Pharm. Sci.*, 61, 723, 1972.
34. **Ostrenga, J. A.,** On the additivity of molar attraction constants, *J. Pharm. Sci.*, 58, 1281, 1969.
35. **Hoy, K. L.,** New values of the solubility parameters from vapor pressure data, *J. Paint Technol.*, 42(541), 76 and 115, 1970.
36. **Hoy, K. L.,** *Tables of Solubility Parameters*, Union Carbide Corporation, Chemicals and Plastics Research and Development Dept., South Charleston, WV, 1969, 1975, and 1985.
37. **Matsuura, T.,** Reverse osmosis separation of solute from aqueous solution, *Yukui Gosei Kagaku Kyokai (J. Syn. Org. Chem. Jpn.)*, 31, 717, 1973.
38. **Hoftyzer, P. J. and van Krevelen, D. W.,** Paper IIIa-15, *Int. Symp. Macromol. (IUPAC), Leyden*, 1970.
39. **van Krevelen, D. W.,** Chemical structure and properties of coal. XXVIII — Coal constitution and solvent extraction, *Fuel*, 44, 229, 1965.
40. **Chavan, R. B., Venkata Rao, J., and Ahmad, A.,** Solubility parameters for dyeing water swollen, solvent exchanged cotton with anionic dyes from mixed solvents, *Text. Res. J.*, 53, 347, 1983.
41. **McGowan, J. C.,** The estimation of solubility parameters and related properties of liquids, *J. Chem. Tech. Biotechnol.*, 34A, 38, 1984.
42. **Boberski, W. G., Seiner, J. A., and Petracca, V. G.,** Reducing the viscosity of magnesia cement with organosilicon compounds, *Ind. Eng. Chem. Prod. Res. Dev.*, 21, 531, 1982.
43. **Fisher, C. H.,** Equations correlate *n*-alkane physical properties with chain length, *Chem. Eng.*, 89(19), 111, 1982.
44. **Scatchard, G.,** Equilibrium in nonelectrolyte mixtures, *Chem. Rev.*, 44, 7, 1949.
45. **Exner, O.,** Additive physical properties. I. Relations and problems of statistical nature, *Collect. Czech. Chem. Commun.*, 31, 3222, 1966.
46. **Brower, K. R., Peslak, J., Jr., and Elrod, J.,** A correlation of molecular flexibility with volume and heat of mixing of organic solutes with water and glycol-water mixture, *J. Phys. Chem.*, 73, 207, 1969.
47. **Askadskii, A. A.,** Influence of chemical structure on the properties of polymers, *Pure Appl. Chem.*, 46, 19, 1976.
48. **Askadskii, A. A.,** Computational procedures for the determination of the physical characteristics of polymers, *Usp. Khim.*, 46, 1122, 1977; *Russ. Chem. Rev.*, 46, 589, 1977.
49. **Askadskii, A. A., Kolmakova, L. K., Tager, A. A., Slonimskii, G. L., and Korshak, V. V.,** Evaluation of solubility parameters of low-molecular-weight liquids and polymers, *Dokl. Akad. Nauk SSR*, 226, 857, 1976; *Dokl. Phys. Chem.*, 226, 99, 1976.
50. **Askadskii, A. A., Kolmakova, L. K., Tager, A. A., Slonimskii, G. L., and Korshak, V. V.,** Estimation of cohesion energy of low-molecular-weight liquids and polymers, *Vysokomol. Soedin. Ser. A*, 19, 1004, 1977; *Polym. Sci. U.S.S.R.*, 19, 1159, 1977.
51. **Kaelble, D. H.,** *Physical Chemistry of Adhesion*, John Wiley & Sons-Interscience, New York, 1971.
52. **Moriguchi, I., Kanada, Y., and Komatsu, K.,** Quantitative structure-activity studies. II. van der Waals volume and the related parameters for hydrophobicity in structure-activity studies, *Chem. Pharm. Bull.*, 24, 1799, 1976.
53. **Peiffer, D.,** The molecular factors affecting the solubility parameter, *J. Appl. Polym. Sci.*, 25, 369, 1980.
54. **Drahos, J.,** Liquid-vapor equilibrium. LXXVII. Comparison of the volume and surface modifications of the regular solution model, *Collect. Czech. Chem. Commun.*, 43, 805, 1978; **Drahos, J., Wichterle, I., and Hala, E.,** A generalized method for calculation and prediction of vapour-liquid equilibria at high pressures, *Fluid Phase Equil.*, 1, 173, 1977—1978.
55. **Erdös, E.,** Liquid-vapor equilibriums. XV. Calculation of the constants in the van Laar equation from the properties of the pure components, *Collect. Czech. Chem. Commun.*, 21, 1528, 1956.
56. **Sokolova, S. P. and Pereverzev, A. N.,** Solubility parameters of individual n-alkanes, *Zh. Fiz. Khim.*, 51, 1267, 1977; *Russ. J. Phys. Chem.*, 51, 750, 1977; *Deposited Doc. VINITI*, 472—477, 1977.
57. **Rätzsch, M. and Krahn, G.,** Excess functions in polymer solutions, *J. Polym. Sci. Polym. Symp.*, 42, 1001, 1973.

58. **Watanabe, A. and Sugiyama, S.,** Relation between molecular weight and solubility parameter for pure organic liquids, *Kogyo Kagaku Zasshi*, 72, 1195, 1969.
59. **Konstam, A. H. and Feairheller, W. R., Jr.,** Calculation of solubility parameters of polar compounds, *Am. Inst. Chem. Eng. J.*, 16, 837, 1970.
60. **Jayasri, A. and Yaseen, M.,** Solubility parameter values suggested using the reported and calculated values for organic compounds, *J. Oil Colour. Chem.*, 63(2), 61, 1980.
61. **Wolf, B. A.,** An extrapolation method for the determination of solubility parameters of polymers demonstrated for polyethylene, *Makromol. Chem.*, 178, 1869, 1977.
62. **Wiehe, I. A. and Bagley, E. B.,** Estimation of dispersion and hydrogen bonding energies in liquids, *Am. Inst. Chem. Eng. J.*, 13, 836, 1967.
63. **Fisher, C. H.,** Equations for calculating homolog solubility parameters: The limiting solubility parameter, *J. Coatings Technol.*, 54(688), 67, 1982.
64. **Fisher, C. H.,** Calculating solubility parameters from their molar products and molar quotients, *Polym. Mater. Sci. Eng.*, 51, 588, 1984.
65. **Fisher, C. H.,** Equations for calculating homolog solubility parameters. II. Simple equations based on chain length, *J. Coatings Technol.*, 57(724), 69, 1985.
66. **Rawat, B. S. and Gulati, I. B.,** Cohesive energy density of polar and non-polar liquids, *J. Appl. Chem. Biotechnol.*, 27, 459, 1979.
67. **Brown, H. C., Barbaras, G. K., Bernels, H. L., Bonner, W. H., Johannensen, R. B., Grayson, M., and Nelson, K. L.,** Strained homomorphs. 14. General summary, *J. Am. Chem. Soc.*, 75, 1, 1953.
68. **Bondi, A. and Simkin, D. J.,** On the hydrogen bond contribution to the heat of vaporization of aliphatic alcohols, *J. Chem. Phys.*, 25, 1073, 1956.
69. **Bondi, A. and Simkin, D. J.,** Heats of vaporization of hydrogen-bonded substances, *Am. Inst. Chem. Eng. J.*, 3, 473, 1957.
70. **Anderson, R.,** Ph.D. Thesis, Dept. of Chemical Engineering, University of California, Berkeley, CA, 1961.
71. **Prausnitz, J. M. and Anderson, R.,** Thermodynamics of solvent selectivity in extractive distillation of hydrocarbons, *Am. Inst. Chem. Eng. J.*, 7, 96, 1961.
72. **Blanks, R. F. and Prausnitz, J. M.,** Volumetric properties of gas mixtures containing one or more polar components, *Am. Inst. Chem. Eng. J.*, 8, 86, 1962.
73. **Blanks, R. F. and Prausnitz, J. M.,** Thermodynamics of polymer solubility in polar and nonpolar systems, *Ind. Eng. Chem. Fundam.*, 3, 1, 1964.
74. **Weimer, R. F. and Prausnitz, J. M.,** Screen extraction solvents this way, *Hydrocarbon Process. Petr. Ref.*, 44, 237, 1965.
75. **Hildebrand, J. H., Prausnitz, J. M., and Scott, R. L.,** *Regular and Related Solutions*, Van Nostrand — Reinhold, Princeton, NJ, 1970.
76. **Hansen, C. M. and Beerbower, A.,** Solubility parameters, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Suppl. Vol., Standen, A., Ed., Interscience, New York, 1971, 889.
77. **Thompson, R. W.,** Ph.D Thesis, Dept. of Chemical Engineering, University of California, Berkeley, CA, 1972.
78. **Helpinstill, J. G. and Van Winkle, M.,** Prediction of infinite dilution activity coefficients for polar-polar binary systems, *Ind. Eng. Chem. Proc. Des. Dev.*, 7, 213, 1968.
79. **Wingefors, S.,** *Studies of the Solvent Extraction Chemistry of Dialkyldithiophosphates and Development of Models for Non-Ideal Behavior in Solvent Extraction*, Thesis, Dept. of Nuclear Chemistry, Chalmers University of Technology, Göteborg, Sweden, 1979.
80. **Wingefors, S. and Liljenzin, J. O.,** Cohesion energy densities and solubility parameters for the n-alkanes expressed as a new homomorph equation, *J. Chem. Technol. Biotechnol.*, 31, 523, 1981.
81. **Beerbower, A. and Dickey, J. R.,** Advanced methods for predicting elastomer/fluids interactions, *Am. Soc. Lubric. Eng. Trans.*, 12, 1, 1969.
82. **Hansen, C. M.,** *Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient. Importance in Surface Coating Formulation*, Doctoral Dissertation, Danish Technical Press, Copenhagen, 1967.
83. **Hansen, C. M.,** The three dimensional solubility parameter — key to paint component affinities. I. Solvents, plasticizers, polymers and resins. II. Dyes, emulsifiers, mutual solubility and compatibility, and pigments, *J. Paint Technol.*, 39, 104 and 505, 1967.
84. **Beerbower, A.,** Surface free energy: a new relationship to bulk energies, *J. Colloid Interface Sci.*, 35, 126, 1971.
85. **Beerbower, A. and Nixon, J.,** Properties of high-internal-phase emulsions. II. Theory of emulsifier selection, *Am. Chem. Soc. Div. Pet. Chem. Prepr.*, 14(1), 62, 1969.
86. **Zisman, W. A.,** Relation of the equilibrium contact angle to liquid and solid constitution, in *Contact Angle, Wettability and Adhesion*, (*Adv. Chem. Ser.* 43), American Chemical Society, Washington, D.C., 1964, chap. 1.

rameter for pure
ılar compounds,
l and calculated
polymers dem-
in liquids, *Am.*
ility parameter,
ıtients, *Polym.*
ions based on
. *Appl. Chem.*
Grayson, M.,
1, 1953.
n of aliphatic
Inst. Chem.
erkeley, CA,
listillation of
r more polar
ılar systems,
ocess. Petr.*
ın Nostrand
f Chemical
keley, CA,
polar-polar
velopment
Chalmers
n-alkanes
ons, *Am.*
portance
967.
Solvents,
igments,
Sci., 35,
nulsifier
t Angle,
, 1964,

---

87. **Loev, A. M. and Lavrishchev, L. P.,** Method for the selection of solvents for coating materials, *Lakokras. Mater. Ikh. Primen.*, No. 4, 4, 1977.
88. **Stekol'shchikov, M. N., Krivtsova, L. M., and Ratner, M. I.,** Evaluation of the dissolving ability of hydrocarbon solvents, *Khim. Tekhnol. Topl. Masel*, No. 6, 33, 1987; *Chem. Technol. Fuels Oils*, No. 6, 292, 1987.
89. **Martin, A., Wu, P. L., Adjei, A., and Beerbower, A.,** Extended Hansen solubility approach — naphthalene in individual solvents, *J. Pharm. Sci.*, 70, 1260, 1981.
90. **Wu, P. L., Beerbower, A., and Martin, A.,** Extended Hansen solubility approach — calculating partial solubility parameters of solid solutes, *J. Pharm. Sci.*, 71, 1285, 1982.
91. **Koenhen, D. M., Mulder, M. H. V., and Smolders, C. A.,** Phase separation phenomena during the formation of asymmetric membrane, *J. Appl. Polym. Sci.*, 21, 199, 1977.
92. **Meusberger, K. E.,** Determination of cohesive energy parameters for pesticide formulation development, *Am. Chem. Soc. Symp. Ser.*, 371(Pesticide Formulations), 151, 1988.
93. **Ostrenga, J. A.,** Correlation of biological activity with chemical structure. Use of molar attraction constants, *J. Med. Chem.*, 12, 349, 1969.
94. **Ostrenga, J. A. and Steinmetz, C.,** Estimation of steroid solubility: use of fractional molar attraction constants, *J. Pharm. Sci.*, 59, 414, 1970.
95. **Ahmad, H. and Yaseen, M.,** Estimation of the solubility parameters of low molecular weight compounds by a chemical group contribution technique, *J. Oil Col. Chem. Assoc.*, 60, 99, 1977.
96. **Ahmad, H. and Yaseen, M.,** Principle of additivity of chemical group, atom, and bond used for determination of solubility parameters, *Paintindia*, 30(4), 3, 1980.
97. **Jayasri, A. and Yaseen, M.,** Heat of vaporization: its determination and application in evaluation of solubility parameter: a review, *Prog. Org. Coat.*, 7, 167, 1979.
98. **Qian, X., Lin, Y., and Ren, S.,** Calculation and application of the solubility parameter of disperse dyes, *Huadong Huagong Xueyan Xuebao*, 13, 573, 1987.
99. **Abrams, D. S. and Prausnitz, J. M.,** Statistical thermodynamics of liquid mixtures. New expression for the excess Gibbs energy of partly or completely miscible systems, *Am. Inst. Chem. Eng. J.*, 21, 116, 1975.
100. **Fredenslund, A., Jones, R. L., and Prausnitz, J. M.,** Group-contribution estimation of activity coefficients in nonideal liquid mixtures, *Am. Inst. Chem. Eng. J.*, 21, 1086, 1975.
101. **Varushchenko, R. M., Loseva, O. L., and Druzhinina, A. I.,** Energies of evaporation of dichloroalkanes, *Zh. Fiz. Khim.*, 62, 2329, 1988; *Russ. J. Phys. Chem.*, 62, 1204, 1988.
102. **Sears, J. K. and Darby, J. R.,** *The Technology of Plasticizers*, Wiley-Interscience, New York, 1982.
103. **Samaha, M. W. and Naggar, V. F.,** Micellar properties of non-ionic surfactants in relation to their solubility parameters, *Int. J. Pharm.*, 42, 1, 1988.
104. **Pussemier, L., De Borger, R., Cloos, P., and Van Bladel, R.,** Relation between the molecular structure and the adsorption of arylcarbamate, phenylurea and anilide pesticides in soil and model organic adsorbents, *Chemosphere*, 18, 1871, 1989.