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An Empirical Equation of State for Liquids

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An empirical four-parameter equation is presented. It has been applied to 104 compounds in the liquid state, and it allows experimental specific volumes of liquids up to 300 MPa to be interpolated quite well at least in the temperature domain approximately ranging from melting to boiling at atmospheric pressure. In particular, results for saturated hydrocarbons, alcohols, esters, glycols, and alkyl halides have been considered. In each family of compounds, the four parameters were found not to vary much. It was then possible to characterize each family by mean values of two parameters. Using these two parameters together with two volume data determined at atmospheric pressure, it was possible to predict specific volumes of liquids up to 300 MPa with a 1% accuracy for the last four families quoted above. The results for saturated hydrocarbons are more scattered (in the 2% range), but this extrapolating method is surely a useful one when high-pressure data are lacking.

Introduction

The van der Waals equation (*1*) is able to represent qualitatively the p,V,T properties of liquids, particularly in regions near the critical point. However, it was necessary to develop other p,V,T equations to correctly describe the variation of the specific volume as a function of pressure at high pressures (up to and over 100 MPa), within temperature ranges well below the critical temperature, for instance in the domain ranging from the melting temperature to the boiling point at atmospheric pressure.

These equations are empirical, like that presented by Tumlirz (*2*); that is

$$V - b = \frac{cT}{B + p} \tag{1}$$

Some years before, Tait (*3*) had proposed an equation to calculate the compressibility of sea water from density data; it can be written as

$$\frac{V - V_0}{V_0 p} = -\frac{A}{B + p} \tag{2}$$

where V_0 is the volume at zero pressure and A and B are positive parameters. The very popular equation

$$\frac{V - V_0}{V_0} = C \ln \frac{B}{B + p} \tag{3}$$

usually referred to as the Tait equation, is the integrated form of a compressibility equation suggested by Tammann (*4*).

The Tait–Tammann equation is most often used to fit p,V,T data of liquids; this is also the case for Hudleston's (*5*) and Hayward's (*6*) relations. The quantities B and C and the volume V_0 are generally considered as polynomial functions of temperature in order to handle simultaneously all the p,V,T data. In Lyons and Scaife's work (*7*), such a modified Tait–Tammann equation is used to fit p,V,T data corresponding to six linear hydrocarbons.

However, a great number of empirical parameters are usually necessary to fit the experimental results. Even the equation recently presented by Cho (*8*), which fits very well many experimental results, contains nine parameters.

An Empirical Four-Parameters Equation

For this reason, we looked for a simpler p,V,T equation able to reproduce the volume variations of all liquids within experimental uncertainty in a large pressure domain and to temperatures not higher than the temperature of the boiling point at atmospheric pressure. The relation can be written as

$$V = \frac{a + bp}{c - dT + p} \tag{4}$$

where V is the specific volume, p is the pressure, T is the temperature, and $a, b, c,$ and d are positive empirical constants; b represents the specific volume at infinite pressure whereas d can be considered as related to the molecular dynamics of liquids. Equation 4 was suggested by the shapes of the V vs p experimental curves. It has already been used in a previous paper (*9*) to fit our p,ρ,T results on cyclohexane and, in slightly modified forms, those on n-heptane and on the cyclohexane + n-heptane equimolar mixture. Eq 4 yields the following expression for p:

$$p = \frac{dVT}{V - b} - \frac{cV - a}{V - b} \tag{5}$$

As pointed out by Bridgman (*10*), in such a relation pressure can be regarded as generated by two different mechanisms, the first one arising from molecular dynamics (dynamic pressure) and the second one from the attractive and the repulsive molecular forces (static or internal pressure): they correspond to the T-dependent term and the T-independent one, respectively. The expression of the internal pressure $(\partial U/\partial V)_T$ is very similar to that proposed by Geissler (*11*); that is

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{s}{(V - b)^n} \tag{6}$$

where s and n are two constants.

In our case, n is equal to 1 and s is an increasing linear function of the specific volume which becomes zero at $V = a/c$, which is also the volume along the isochore going through

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Table I. Parameters *a* ($cm^3 \cdot g^{-1} \cdot MPa$), *b* ($cm^3 \cdot g^{-1}$), *c* (MPa), and *d* ($MPa \cdot K^{-1}$) and Average and Maximum Percentage Deviations Δ_{AVE} and Δ_{MAX} for Representation of Experimental Results on Specific Volume ($cm^3 \cdot g^{-1}$) from References in the Literature by Equation 4[a]

substance or mixture	*P*/MPa	*T*/K	*a*	*b*	*c*	*d*	Δ_{AVE}	Δ_{MAX}	ref
ethane I	0.5–40.8	93–184	271.15	1.3949	204.78	0.3078	0.05	0.22	18
ethane II	0.5–69.4	93–304	52.810	1.7027	46.530	0.0977	1.72	8.58	18
ethane III	0.5–69.4	184–304	50.690	1.7398	49.270	0.1104	1.08	6.68	18
propane I	1–37.5	90–220	276.03	1.2437	227.30	0.2876	0.04	0.16	19
propane II	1–37.5	90–300	147.96	1.3497	124.25	0.1704	0.31	1.36	19
butane I	1.7–36.1	140–260	210.72	1.2402	183.05	0.2061	0.04	0.16	20
butane II	1.7–36.1	140–300	170.98	1.2787	149.67	0.1732	0.10	0.34	20
2-methylpropane I	1.7–34.7	120–260	203.20	1.2488	174.00	0.2033	0.05	0.19	21
2-methylpropane II	1.7–34.7	120–300	167.81	1.2796	144.71	0.1739	0.13	0.65	21
pentane	0–981	273–368	560.75	0.9694	469.45	0.3691	0.33	1.86	31
2-methylbutane	0.1–203	223–298	249.91	1.1645	221.48	0.2255	0.10	0.42	25
	0–883	273–368	484.94	1.0189	409.78	0.3450	0.30	1.58	31
hexane	0.1–196	298–353	268.03	1.1228	241.50	0.2230	0.09	0.30	17
	0.1–203	223–298	294.15	1.1126	265.01	0.2412	0.08	0.29	24
	0.1–564	298–373	406.76	1.0409	276.27	0.3237	0.29	1.25	36
	0–1079	273–368	527.62	0.9790	457.10	0.3656	0.36	1.67	31
2-methylpentane	0–1177	273–368	522.90	0.9786	449.34	0.3496	0.48	2.77	31
3-methylpentane	0–1177	273–368	561.70	0.9447	495.15	0.3889	0.61	3.24	31
2,2-dimethylbutane	0–981	273–368	502.54	1.0206	420.09	0.2942	0.31	1.00	31
2,3-dimethylbutane	0–1079	273–368	499.35	0.9711	433.43	0.3355	0.49	2.50	31
heptane	0.1–100	298–373	175.70	1.2052	163.43	0.1490	0.09	0.39	26
	0–118	273–393	209.86	1.1698	197.98	0.1858	0.16	0.47	12
	0.1–196	298–353	252.59	1.1189	231.08	0.2013	0.11	0.34	17
	0.1–263	198–311	354.58	1.0553	323.79	0.2748	0.08	0.58	13
	0–1079	273–368	494.93	0.9607	441.94	0.3519	0.52	2.27	31
3-ethylpentane	0.1–196	298–353	253.85	1.1029	238.33	0.2107	0.09	0.31	17
octane	0–118	303–393	199.82	1.1599	188.37	0.1642	0.10	0.54	12
	0.1–460	298–348	390.62	1.0168	359.90	0.2905	0.26	0.83	37
	0–981	273–368	484.69	0.9676	443.23	0.3491	0.43	1.48	31
2,2,4-trimethylpentane (isooctane)	0.1–540	298–373	346.03	1.0310	323.33	0.2830	0.33	1.49	39
	0–981	273–368	497.45	0.9657	435.20	0.2986	0.39	1.92	32
nonane	0–118	303–393	202.43	1.1503	191.46	0.1581	0.07	0.39	12
3,3-diethylpentane	0–800	303–423	418.37	0.9498	392.42	0.2522	0.29	3.09	35
decane	0–300	298–383	345.50	1.0285	321.50	0.2386	0.10	0.82	28
	0–785	273–368	448.16	0.9647	415.25	0.3007	0.37	1.03	31
dodecane	0–118	303–393	226.23	1.1111	217.44	0.1642	0.05	0.20	12
	0.1–442	298–373	378.10	1.0000	357.48	0.2548	0.15	0.54	37
hexadecane	0–118	303–393	250.77	1.0803	244.50	0.1725	0.04	0.13	12
heptadecane	0–800	303–453	452.98	0.9429	426.64	0.2600	0.26	2.32	35
squalane[b]	0.1–196	298–353	363.31	0.9768	357.74	0.2199	0.04	0.10	17
7-hexyltridecane	0.1–340	311–408	329.53	0.9965	318.19	0.2037	0.14	0.54	29
11-decylheneicosane	0.1–340	311–408	314.33	0.9981	314.06	0.2022	0.17	0.79	29
13-dodecylhexacosane	0.1–340	311–408	364.79	0.9708	361.37	0.2159	0.09	0.31	29
0.5 octane + 0.5 dodecane	0.1–413	298–373	365.93	1.0186	347.86	0.2742	0.22	0.54	37
0.5 isooctane + 0.5 dodecane	0.1–605	298–373	385.56	1.0021	372.53	0.3093	0.29	0.76	39
0.5 octane + 0.5 isooctane	0.1–499	298–373	352.61	1.0217	319.56	0.2539	0.28	1.65	41
0.5 decane + 0.5 tetradecane	0.1–430	298–358	348.23	1.0208	329.57	0.2372	0.12	0.31	46
0.5 dodecane + 0.5 hexadecane	0.1–331	298–358	333.27	1.0223	320.86	0.2281	0.06	0.50	46
0.6 decane + 0.2 tetradecane + 0.2 hexadecane	0.1–359	298–358	334.71	1.0285	317.60	0.2296	0.09	0.34	46
cyclopentane	0.1–196	298–353	278.60	1.0068	271.40	0.2196	0.06	0.17	17
cyclohexane	0.1–85	288–323	220.45	1.0435	230.85	0.2022	0.02	0.07	14
	0.1–102	292–343	207.36	1.0573	216.14	0.1873	0.06	0.19	9
	0.1–110	287–338	203.06	1.0574	214.13	0.1914	0.05	0.20	16
	0.1–214	313–383	231.71	1.0273	239.61	0.2039	0.10	0.54	44
methylcyclohexane	0.1–500	203–298	444.17	0.9252	447.07	0.3550	0.15	0.45	43
trans-decalin	0.1–196	298–353	334.19	0.9088	357.60	0.2311	0.05	0.12	17
perhydrochrysene[d]	0.1–340	311–408	379.87	0.8334	435.60	0.2189	0.06	0.18	29
1,1-Di-α-decalylhendecane	0.1–300	311–408	359.44	0.8829	398.26	0.2168	0.07	0.20	29
0.5 cyclohexane + 0.5 heptane	0.1–100	298–353	175.26	1.1497	166.86	0.1388	0.09	0.38	9
oct-1-ene	0.1–313	298–373	293.44	1.0583	285.01	0.2535	0.17	0.50	40
squalene[c]	0.1–196	298–353	392.15	0.9216	410.58	0.2570	0.03	0.09	17
0.5 oct-1-ene + 0.5 octane	0.1–412	298–373	339.34	1.0341	323.30	0.2801	0.24	0.70	41
0.5 oct-1-ene + 0.5 isooctane	0.1–291	298–373	273.96	1.0642	259.87	0.2282	0.19	0.60	41
0.333 oct-1-ene + 0.333 octane + 0.333 isooctane	0.1–415	298–373	313.49	1.0504	291.77	0.2443	0.24	0.92	41
benzene	0.1–40.1	298–348	155.13	0.9909	186.68	0.1713	0.03	0.10	38
	0.1–170	288–323	262.08	0.8943	308.77	0.2680	0.03	0.11	14
	0.1–391	298–373	305.76	0.8597	361.47	0.3176	0.14	0.47	38
hexadeuteriobenzene	0.1–454	303–433	280.91	0.8767	330.96	0.2909	0.22	0.85	42
toluene	0.1–203	223–298	332.55	0.8767	377.76	0.3049	0.05	0.11	25
	0.1–263	182–320	346.10	0.8684	393.16	0.3176	0.09	0.30	13
	0.1–459	298–373	359.70	0.8522	403.65	0.3146	0.18	0.74	40
1,1-diphenylethane	0.1–340	311–372	378.68	0.7940	460.39	0.2820	0.09	0.38	29
1,1-diphenylheptane	0.1–340	311–408	356.27	0.8410	407.67	0.2386	0.11	0.60	29
1,1-diphenyltetradecane	0.1–340	311–408	328.17	0.8873	365.58	0.2184	0.11	0.29	29
bixylyltoluene[d]	0.1–196	298–353	380.36	0.8814	412.01	0.2350	0.03	0.06	17

Table I (Continued)

substance or mixture	P/MPa	T/K	a	b	c	d	Δ_{AVE}	Δ_{MAX}	ref
1,2,3,4,5,6,8,13,14,15,16-dodecahydrochrysene[d]	0.1–340	311–408	380.80	0.7896	470.18	0.2420	0.04	0.09	29
diethyl ether	0.1–1177	293–353	600.99	0.8439	563.99	0.4326	0.38	2.64	30
furan	11–897	209–257	551.00	0.6944	668.98	0.4735	0.13	1.36	45
anisole (methoxybenzene)	0.1–196	298–353	321.05	0.7949	404.94	0.2942	0.04	0.14	17
1-(methoxyphenyl)-1-phenylethane[d]	0.1–196	298–353	364.97	0.7768	456.55	0.2598	0.03	0.08	17
1-(methoxycyclohexyl)-1-cyclohexylethane[d]	0.1–196	298–353	367.03	0.8584	413.74	0.2445	0.04	0.11	17
2,4-bis(α-phenylethyl)phenyl ethyl ether[d]	0.1–196	298–353	366.04	0.7694	459.09	0.2465	0.03	0.12	17
2,4-bis(α-cyclohexylethyl)cyclohexyl methyl ether[d]	0.1–196	298–353	358.22	0.8322	409.51	0.2236	0.04	0.13	17
methanol	0.1–1177	293–353	593.61	0.8108	611.79	0.4737	0.26	1.36	30
ethanol	0.1–1177	293–353	627.23	0.8035	628.81	0.4449	0.32	1.77	30
propan-1-ol	0.1–1177	293–353	554.03	0.8597	563.06	0.3934	0.34	1.76	30
propan-2-ol	0.1–1177	273–368	587.95	0.8492	589.83	0.4300	0.35	1.63	31
butan-1-ol	0.1–1177	273–368	610.50	0.8419	610.64	0.3930	0.29	1.03	31
2-methylpropan-1-ol	0.1–1177	293–353	567.12	0.8301	583.08	0.4238	0.31	1.70	30
2-methylbutan-2-ol	0.1–1177	293–353	587.22	0.8307	595.96	0.3927	0.32	1.57	30
octan-3-ol	0.1–1177	273–368	635.68	0.8356	643.24	0.4018	0.23	1.12	33
3-methylheptan-1-ol	0.1–1177	273–368	686.76	0.8246	688.35	0.3954	0.22	1.19	33
2-methylheptan-3-ol	0.1–1177	273–368	649.10	0.8247	664.56	0.4319	0.29	1.24	33
3-methylheptan-4-ol	0.1–1177	273–368	635.58	0.8305	650.03	0.4076	0.25	1.33	33
2-methylheptan-5-ol	0.1–1177	273–368	639.62	0.8329	645.63	0.4028	0.27	1.27	33
cyclopentanol	0.1–230	273–325	283.66	0.8731	340.08	0.2443	0.10	0.29	16
1,2-ethanediol	0–1177	273–368	828.14	0.6362	1086.4	0.5566	0.10	0.37	32
1,2-propanediol	0–1177	273–368	906.19	0.6588	1117.6	0.5948	0.20	0.62	32
1,3-propanediol	0–1177	273–368	765.10	0.6864	950.16	0.4882	0.12	0.43	32
2,2-oxydiethanol	0–1177	273–368	794.67	0.6439	1038.3	0.5112	0.13	1.13	32
1,2,3-propanetriol	0–1177	273–368	1165.8	0.5711	1639.2	0.7077	0.12	0.36	32
propan-2-one	0.1–1177	293–353	610.06	0.7935	626.11	0.4842	0.27	1.95	30
cyclohexanone	0.1–220	253–303	338.34	0.8374	405.13	0.2901	0.07	0.23	16
glycerol triacetate	0–1177	273–368	596.28	0.5900	870.17	0.5301	0.18	0.66	32
glycerol trihexanoate	0–1177	273–368	620.48	0.7073	736.56	0.4248	0.17	0.86	32
butyl phthalate[d]	0–1177	273–368	626.44	0.6703	786.82	0.4320	0.17	0.66	32
methyl oleate[d]	0–981	273–368	632.50	0.8005	671.67	0.3846	0.21	0.57	32
dibenzyl ethylmalonate[d]	0–490	273–368	438.00	0.7024	579.31	0.3332	0.12	0.35	32
chloroethane	0.1–1177	293–353	450.43	0.6846	549.06	0.4767	0.35	1.78	30
1-chloropropane	0–1177	273–368	533.77	0.6954	635.80	0.5081	0.32	1.65	33
1-chlorobutane	0–1177	273–368	520.83	0.7258	593.05	0.4347	0.35	1.76	33
1-chloropentane	0–1177	273–368	535.82	0.7273	608.01	0.4261	0.31	1.93	33
chlorobenzene	0–1079	273–368	390.21	0.6662	543.11	0.3797	0.24	0.93	31
bromoethane	0.1–1177	293–353	352.93	0.4284	667.75	0.4835	0.23	2.06	30
1-bromopropane	0–1177	273–368	366.72	0.4736	637.82	0.4780	0.33	1.94	33
1-bromobutane	0–1177	273–368	395.46	0.5069	642.62	0.4545	0.31	1.85	33
1-bromopentane	0–1177	273–368	417.12	0.5382	637.04	0.4195	0.25	1.64	33
bromobenzene	0–883	273–368	319.11	0.4817	591.69	0.3922	0.20	0.73	31
iodoethane	0.1–1177	293–353	247.22	0.3335	602.85	0.4170	0.32	1.62	30
1-iodopropane	0–1177	273–368	325.21	0.3686	711.92	0.4763	0.28	1.41	33
1-iodobutane	0–1177	273–368	352.72	0.4030	706.86	0.4567	0.27	1.33	33
1-iodopentane	0–1177	273–368	364.45	0.4237	690.39	0.4308	0.26	1.54	33
hexafluorobenzene	0.1–40.1	298–348	76.789	0.5213	176.02	0.1769	0.02	0.11	38
	0.1–310	298–373	111.69	0.4877	253.22	0.2490	0.18	0.57	38
acetonitrile	10–300	283–313	372.62	0.9157	395.60	0.3566	0.09	0.25	15
2,2′,2″-trihydroxytriethylamine	0–981	273–368	712.51	0.6398	938.73	0.4121	0.09	0.22	33
formamide	0.1–280	288–323	562.91	0.6652	779.27	0.4813	0.02	0.05	27
Tri-*o*-cresyl phosphate[d]	0–588	273–368	473.79	0.6595	654.61	0.3189	0.05	0.13	32
tetramethylsilane	0.1–102	198–298	186.09	1.1540	173.41	0.1849	0.07	0.34	23
	4.5–455	298–373	282.13	1.0325	254.03	0.2449	0.31	1.16	42
tetrachloromethane	0.1–198	273–323	145.14	0.4808	311.37	0.2729	0.06	0.15	25
carbon disulfide	0.1–102	198–298	207.11	0.6068	349.53	0.2991	0.04	0.13	22
	0.1–203	223–298	245.46	0.5835	412.70	0.3494	0.05	0.13	25
	0.1–1177	293–353	423.43	0.5051	684.04	0.4980	0.23	1.20	30
phosphorus trichloride	0.1–1177	293–353	309.01	0.4228	626.27	0.4692	0.29	1.76	30
water	0–800	298–363	876.52	0.6507	1050.9	0.5689	0.13	0.84	34
	0–1079	273–368	672.62	0.6907	797.48	0.4355	0.33	0.90	31

[a] $\Delta_{AVE} = 10^2 \langle \delta V/V \rangle_{AVE}$ and $\Delta_{MAX} = 10^2(\delta V/V)_{MAX}$, where δV is the absolute difference between experimental and calculated specific volumes V from eq 4. [b] 2,6,10,15,19,23-Hexamethyltetracosane. [c] 2,6,10,15,19,23-Hexamethyl-2,6,10,14,18,22-tetracosahexaene. [d] Structural formula reported in ref 32.

the point ($P = 0$, $T = 0$) according to eq 4: along this isochore, c can be viewed as the absolute value of each of the opposing attractive and repulsive pressures and a can be considered as a constant configurational energy.

The dynamic pressure term of eq 5 may be expressed as the sum of two contributions; that is

$$\frac{dVT}{V-b} = dT + \frac{bdT}{V-b} \qquad (7)$$

Equation 5 predicts the increase of thermal expansivity when temperature increases while neither a relation such as

$$p = \frac{dT}{V-b} - \frac{cV-a}{V-b} \qquad (8)$$

in which the T-dependent term has the same form as in the van der Waals relation nor Tumlirz equation does. Besides, our equation accounts for the increase of isothermal compressibility with increasing temperature. We think that these features which are characteristic of the general behavior of liquids have to be contained in a fair equation of state.

We have considered many types of organic liquids, in order to take into account several functional groups. We also aimed

Table II. Experimental Uncertainties (%), Δ_{EXP}, on Specific Volume Measurements Affecting the Results Used for Our Correlation by Means of Equation 4 and Mean, Δ_{AVE}, and Maximum, Δ_{MAX}, Deviations Calculated for the Compound of Each Series Whose Results Turn out to be the More Poorly Interpolated

	Δ_{EXP}	ref	Δ_{AVE}	Δ_{MAX}	compound	ref
Toscani et al.	0.20	9, 26	0.09	0.39	heptane	26
Boelhouwer	0.04	12	0.16	0.47		12
Trappeniers et al.	0.20[a]	13, 14	0.09	0.30	toluene	13
Würflinger et al.	1	15, 16	0.10	0.29	cyclopentanol	16
Kuss, Tasmili	0.20[a]	17	0.11	0.34	heptane	17
Haynes	0.10	19–21	0.05	0.19	2-methylpropane	21
Garcia Baonza et al.	0.20	22, 23	0.07	0.34	tetramethylsilane	23
Mopsik	0.03	24, 25	0.10	0.42	2-methylbutane	25
Easteal, Woolf	0.02	27	0.02	0.05	formamide	27
Gehring, Lentz	0.14	28	0.10	0.82	decane	28
Lowitz et al.	0.14	29	0.17	0.79	11-decylheneicosane	29
Bridgman	1[a]	30–33	0.61	3.24	3-methylpentane	31
Grindley et al.	0.01	34–35	0.29	3.09	3,3-diethylpentane	35
Dymond et al.	0.20	36–41	0.33	1.49	isooctane	39
Jonas et al.	1	42–44	0.31	1.16	tetramethylsilane	42
Figuière, Szwarc	1	45	0.13	1.36	furan	45
Synder et al.	0.06	46	0.12	0.31	0.5 decane + 0.5 tetradecane	46

[a] Estimated by us.

to treat data arising from a great variety of experimental techniques of density determination at high pressures. Table I shows the values of parameters *a*, *b*, *c*, and *d* as well as the average and maximum deviations between experimental and calculated specific volumes as determined by fitting eq 4 to experimental results. Equation 4 has been fitted to experimental results by means of linear least-squares regressions based upon the Gauss–Jordan matrix inversion algorithm. The lowest degree of freedom is 11 (dibenzyl ethylmalonate (*32*)). On the average, the degree of freedom of our correlation is near 60. No smoothed data have been taken into account, and all experimental points have been assigned the same statistical weight. We have not considered that atmospheric pressure data are more accurate than high-pressure ones, because the same apparatus and methods have been usually used in both cases. Therefore, giving a greater statistical weight to atmospheric pressure data, thus forcing the fitting equations to include them, would not be legitimate. Even Bridgman and Boelhouwer, who use independent data at atmospheric pressure, must follow the same experimental procedure in the whole pressure range: therefore, they only use the atmospheric pressure data as reference values, which does not legitimate any different statistical weight in the correlation process. Average deviations are systematically less than experimental uncertainties for the results from refs 9, 13–17, 19–23, 26, and 28. Measurements reported in refs 29–46 were performed at higher pressures (up to 1200 MPa in the case of Bridgman (*30–33*)). Average deviations are smaller than experimental uncertainties only in the case of Bridgman's, Jonas et al.'s (*42–44*), Figuière and Szwarc's (*45*), and most of Lowitz et al.'s (*29*) results. For the other series, they prove to be slightly higher (for instance, equal to 0.33% for 2,2,4-trimethylpentane to be compared with a 0.2% experimental uncertainty (*39*)). Deviations may become systematic for the highest pressure values or near atmospheric pressure only in the cases of series stretching over a pressure range larger than 300 MPa, such as those investigated by Bridgman. In these cases, however, the mean systematic deviations are not larger than experimental uncertainties. The latter are reported in Table II and arise generally from the estimations of the researchers. When no estimation is given, we have introduced our own, which of course is somewhat arbitrary.

For pressures less than 100 MPa, eq 4 does not lead to good values in the range between boiling and critical point temperatures. As an example, we have reported in Table I three different series of fitted parameters corresponding to volume measurements on ethane collected by Goodwin et al. (*18*): the first one is concerned with measurements performed in the temperature range between the melting and boiling points, the second one corresponds to data up to the critical point temperature, and the third fitting was performed exclusively with data recorded between boiling and critical point temperatures. It can be seen that only the first series gives good results.

Similar conclusions can be drawn as to what concerns the results on propane and on *n*-butane reported by Haynes (*19*, *20*) and those on tetramethylsilane and hexadeuteriobenzene reported by Parkhurst and Jonas (*42*).

From all the calculations, it turns out that eq 4 gives generally better results with globular or highly complex compounds than with linear-chain hydrocarbons or very unsymmetrical branched ones. Better results are also observed for aromatic, heterocyclic, and organic compounds containing polar functional groups. For instance, Figuière and Szwarc (*45*) reported extensive *p*,*V*,*T* measurements on liquid furan from 210 to 260 K up to 1000 MPa; these data are fitted very well by eq 4 in spite of the wide experimental pressure range and of experimental errors that could attain 1%. However, to fairly represent *p*,*V*,*T* behavior within the experimental accuracy from atmospheric to very high pressure in all cases, extra terms depending on *p* will probably be necessary.

The more striking feature of eq 4 lies in the weak variation of most parameters, in particular of *d* and $w = bc/a$, in a given pressure range for compounds belonging to the same chemical family, as can be inferred from Bridgman's series of results reported in Table I. *w* represents the ratio of the volume of the liquid at zero internal pressure to that at infinite pressure. Then, in eq 5, its value should be less than unity.

Nevertheless, we have concentrated on the pressure range extending from 0.1 to 300 MPa since it is common to refs *29–41* and *43* and concerns a fair number of compounds. Furthermore, we feel that it is large enough to yield significant results.

The values of *a*, *b*, *c*, *d*, and *w* as well as the mean errors on specific volumes are reported in Table III for saturated hydrocarbons, alcohols, glycols, esters, and alkyl halides. In this case, the lowest degree of freedom is 6 (*n*-pentane and *n*-hexane (*31*)) while the average one is larger than 20.

The trend suggested in Table I by Bridgman's results is enhanced: in each chemical family, these five parameters do not change much. Considering the most numerous families, which are the saturated hydrocarbons (25 experimental series), the alcohols (12 series), and the alkyl halides (12 series), parameters *d* and *w* are the least scattered ones: the mean scatter for *d* goes from 5.7% (alkyl halides) to 12.3% (saturated hydrocarbons). As for *w*, it varies from 2% (saturated hydrocarbons) to 3.4% (alcohols). Therefore, mean values for *d* and *w*, respectively, have been calculated for saturated hydrocarbons, alcohols, esters, alkyl halides, and glycols.

It must be emphasized that binary mixtures of saturated hydrocarbons have been coped with exactly as neat compounds. The corresponding parameters behave like those of other compounds of this series, and their respective values have been used to determine the mean values of *d* and *w* that will be used in what follows.

The only exception with respect to this behavior is exhibited by 2,2′-oxydiethanol whose *a*, *c*, and *d* values are very different from the respective *a*, *c*, and *d* mean values for the other glycols. The corresponding *d* and *w* values have not been taken into account to calculate the mean values of these parameters for the glycol family. Nevertheless, in what follows, 2,2′-oxydiethanol will be treated as the other members of this family.

Table III. Parameters a ($cm^3 \cdot g^{-1} \cdot MPa$), b ($cm^3 \cdot g^{-1}$), c (MPa), d ($MPa \cdot K^{-1}$), and w and Average Percentage Deviations Δ_{AVE} for Representation, by Equation 4, of the Experimental Results on the Specific Volume ($cm^3 \cdot g^{-1}$) up to 300 MPa from References 29, 30–33, 34, 35, 36–41, and 43

substance or mixture	T/K	a	b	c	d	w	Δ_{AVE}	ref
			Saturated Hydrocarbons					
pentane	273–368	309.94	1.0945	268.00	0.2472	0.9464	0.13	31
2-methylbutane	273–368	306.02	1.1167	264.89	0.2493	0.9666	0.13	31
hexane	298–373	311.54	1.0987	282.35	0.2612	0.9958	0.21	36
	273–368	302.77	1.0958	273.85	0.2543	0.9911	0.15	31
2-methylpentane	273–368	272.82	1.1086	244.37	0.2252	0.9930	0.19	31
3-methylpentane	273–368	253.98	1.0981	232.55	0.2163	1.0054	0.22	31
2,2-dimethylbutane	273–368	288.90	1.1202	251.79	0.2143	0.9763	0.13	31
2,3-dimethylbutane	273–368	278.28	1.0863	250.68	0.2264	0.9786	0.19	31
heptane	273–368	279.46	1.0811	259.30	0.2339	1.0031	0.19	31
octane	298–348	322.39	1.0595	298.16	0.2448	0.9799	0.17	37
	273–368	290.98	1.0743	271.76	0.2309	1.0033	0.21	31
2,2,4-trimethylpentane (isooctane)	298–373	262.32	1.0868	246.71	0.2216	1.0221	0.22	39
	273–368	280.29	1.0737	255.65	0.2099	0.9793	0.13	32
3,3-diethylpentane	303–423	262.92	1.0339	253.63	0.1822	0.9974	0.15	35
decane	273–368	283.35	1.0603	265.31	0.2013	0.9928	0.19	31
dodecane	298–373	329.26	1.0284	313.22	0.2284	0.9783	0.13	37
heptadecane	303–453	295.33	1.0266	284.16	0.1889	0.9878	0.13	35
7-hexyltridecane	311–408	324.79	0.9997	314.27	0.2026	0.9673	0.14	29
11-decylheneicosane	311–408	334.91	0.9873	332.43	0.2090	0.9800	0.14	29
13-dodecylhexacosane	311–408	358.98	0.9739	355.91	0.2133	0.9656	0.09	29
0.5 octane + 0.5 dodecane	298–373	322.53	1.0450	307.29	0.2445	0.9956	0.17	37
0.5 isooctane + 0.5 dodecane	298–373	296.15	1.0529	292.46	0.2584	1.0398	0.26	39
0.5 octane + 0.5 isooctane	298–373	271.89	1.0762	250.01	0.2085	0.9896	0.21	41
methylcyclohexane	203–298	375.15	0.9564	381.50	0.3159	0.9726	0.06	43
perhydrochrysene	311–408	366.83	0.8387	421.08	0.2127	0.9627	0.06	29
			Alcohols					
methanol	293–353	349.47	0.9182	367.88	0.3127	0.9666	0.08	30
ethanol	293–353	339.88	0.9292	348.30	0.2742	0.9522	0.07	30
propan-1-ol	293–353	294.16	0.9632	306.92	0.2412	1.0050	0.04	30
propan-2-ol	273–368	354.63	0.9488	362.53	0.2864	0.9699	0.11	31
butan-1-ol	273–368	385.75	0.9301	392.38	0.2739	0.9461	0.05	31
2-methylpropan-1-ol	293–353	306.31	0.9227	324.12	0.2521	0.9763	0.10	30
2-methylbutan-2-ol	293–353	332.55	0.9302	343.96	0.2503	0.9621	0.06	30
octan-3-ol	273–368	382.30	0.9252	395.93	0.2789	0.9582	0.07	33
3-methylheptan-1-ol	273–368	388.56	0.9241	399.90	0.2661	0.9511	0.07	33
2-methylheptan-3-ol	273–368	258.82	0.9798	282.41	0.2362	1.0691	0.28	33
3-methylheptan-4-ol	273–368	354.99	0.9281	374.49	0.2732	0.9791	0.07	33
2-methylheptan-5-ol	273–368	358.31	0.9320	371.78	0.2674	0.9670	0.05	33
			Glycols					
1,2-ethanediol	273–368	573.94	0.6923	760.53	0.4160	0.9174	0.07	32
1,2-propanediol	273–368	478.49	0.7597	593.38	0.3353	0.9421	0.04	32
1,3-propanediol	273–368	586.37	0.7398	718.68	0.3749	0.9067	0.11	32
2,2′-oxydiethanol	273–368	285.01	0.7632	382.98	0.2258	1.0255	0.25	32
			Esters					
glycerol triacetate	273–368	344.31	0.682	513.16	0.3483	1.0165	0.08	32
glycerol trihexanoate	273–368	389.49	0.7776	469.89	0.2987	0.9381	0.05	32
butyl phthalate	273–368	374.04	0.7411	479.85	0.2982	0.9507	0.05	32
methyl oleate	273–368	357.24	0.8980	389.09	0.2542	0.9781	0.12	32
dibenzyl ethylmalonate	273–368	315.97	0.7454	422.21	0.2556	0.9960	0.04	32
			Alkyl Halides					
chloroethane	293–353	224.31	0.7898	283.19	0.2890	0.9971	0.16	30
1-chloropropane	273–368	301.52	0.7863	366.22	0.3271	0.9550	0.13	33
1-chlorobutane	273–368	283.06	0.8278	333.39	0.2821	0.9750	0.09	33
1-chloropentane	273–368	288.49	0.8282	338.73	0.2770	0.9724	0.13	33
bromoethane	293–353	138.46	0.5241	277.36	0.2659	1.0499	0.10	30
1-bromopropane	273–368	188.26	0.5495	337.23	0.2878	0.9843	0.14	33
1-bromobutane	273–368	208.11	0.5820	347.61	0.2801	0.9721	0.13	33
1-bromopentane	273–368	229.32	0.6112	361.26	0.2761	0.9629	0.11	33
iodoethane	293–353	147.74	0.3757	372.25	0.2955	0.9466	0.08	30
1-iodopropane	273–368	180.23	0.4217	404.02	0.3059	0.9453	0.05	33
1-iodobutane	273–368	197.11	0.4599	402.08	0.2880	0.9381	0.08	33
1-iodopentane	273–368	189.57	0.4885	371.01	0.2731	0.9560	0.14	33

To know whether pairs of mean d and w parameters are really characteristic of given chemical series, we have tested their predictive value. Assuming that such a pair really defines a family, only two data are necessary to determine all four parameters of eq 4. We chose to use two volume measurements performed at atmospheric pressure, being well aware that the results will strongly depend on the accuracies of these measurements. Table IV shows the mean values for d and w which were used for the various chemical families, and the resulting a, b, and c parameters and the mean and maximum errors calculated for each compound.

For alkyl halides, alcohols, glycols, and esters, except for 1-bromopropane, 1-bromobutane, 2-methylheptan-3-ol, 1,3-propanediol, and glycerol triacetate, the maximum errors are systematically less than 1.5% and the mean errors are less than 1.1% even, surprisingly, for 2,2′-oxydiethanol which gives parameters different from those of its chemical family as it was pointed out before (Table III). It was even useless to

Table IV. Parameters *a* (cm^3·g^{-1}·MPa), *b* (cm^3·g^{-1}), and *c* (MPa) Estimated from Mean Values (for Each Chemical Family) for Parameters *d* (MPa·K^{-1}) and *w* in Table II and from a Couple of Specific Volume Data (cm^3·g^{-1}) at Atmospheric Pressure (for Each Substance) by Application of a System of Equations (4) and Average and Maximum Percentage Deviations Δ_{AVE} and Δ_{MAX} on Specific Volume up to 300 MPa for Representation of Experimental Results from References Mentioned in This Table by Equation 4, with the Previously Computed Set of Parameters

substance or mixture	*T*/K	*a*	*b*	*c*	Δ_{AVE}	Δ_{MAX}	ref
Saturated Hydrocarbons: *P*/MPa, 0–300; *w*, 0.9868; *d*, 0.2280							
pentane	273–368	225.23	1.0860	204.65	1.60	2.28	31
2-methylbutane	273–368	219.42	1.0838	199.78	2.19	3.47	31
hexane	298–373	233.02	1.0571	217.53	2.40	3.97	36
	273–368	242.68	1.0701	223.79	2.01	2.60	31
2-methylpentane	273–368	236.77	1.0690	218.57	1.42	2.33	31
3-methylpentane	273–368	235.56	1.0542	220.49	1.23	2.00	31
2,3-dimethylbutane	273–368	238.07	1.0603	221.57	1.15	1.89	31
heptane	273–368	262.74	1.0636	243.77	0.66	1.45	31
octane	298–348	264.21	1.0435	249.84	1.08	1.70	37
	273–368	272.02	1.0515	255.28	0.82	1.58	31
2,2,4-trimethylpentane (isooctane)	298–373	245.48	1.0348	234.10	1.57	2.42	39
	273–368	270.52	1.0615	251.49	0.46	1.45	32
3,3-diethylpentane	303–423	276.43	0.9879	276.14	0.88	2.82	35
decane	273–368	286.99	1.0338	273.94	0.44	0.99	31
dodecane	298–373	300.40	1.0238	289.53	0.39	1.27	37
heptadecane	303–453	314.11	1.0022	309.28	0.71	2.50	35
7-hexyltridecane	311–408	325.85	1.0005	321.38	0.81	1.79	29
11-decylheneicosane	311–408	347.64	0.9884	347.06	0.71	1.41	29
13-dodecylhexacosane	311–408	356.52	0.9860	356.82	0.91	1.31	29
0.5 octane + 0.5 dodecane	298–373	285.01	1.0326	272.37	0.71	1.58	37
0.5 isooctane + 0.5 dodecane	298–373	250.74	0.9991	247.67	2.09	3.53	39
0.5 octane + 0.5 isooctane	298–373	267.80	1.0540	250.73	0.70	1.98	41
methylcyclohexane	203–298	255.13	0.9664	260.51	1.08	1.79	43
perhydrochrysene	311–408	364.65	0.8515	422.60	0.75	1.10	29
hexane[a]	223–298	253.87	1.0832	231.28	0.79	1.53	24
heptane[a]	198–311	263.09	1.0646	243.86	0.77	1.49	13
decane[a]	298–383	285.59	1.0329	272.84	0.55	1.20	28
di-α-decalylhendecane[b]	311–408	362.41	0.8882	402.63	0.75	1.01	29
0.5 decane + 0.5 tetradecane[b]	298–358	299.22	1.0235	288.49	0.65	1.42	46
0.5 dodecane + 0.5 hexadecane[b]	298–358	310.83	1.0170	301.58	0.57	1.24	46
0.6 decane + 0.2 tetradecane + 0.2 hexadecane[b]	298–358	300.16	1.0242	289.21	0.53	1.35	46
Alcohols: *P*/MPa, 0–300; *w*, 0.9752; d, 0.2677							
methanol	293–353	281.94	0.9199	298.88	0.86	1.27	30
ethanol	293–353	299.64	0.9355	312.36	0.26	0.99	30
propan-1-ol	293–353	304.60	0.9263	320.66	0.59	1.15	30
propan-2-ol	273–368	316.48	0.9515	324.38	0.27	0.87	31
butan-1-ol	273–368	359.34	0.9498	368.94	0.93	1.16	31
2-methylpropan-1-ol	293–353	303.31	0.9141	323.59	0.46	1.40	30
2-methylbutan-2-ol	293–353	327.62	0.9318	342.87	0.64	1.04	30
octan-3-ol	273–368	339.82	0.9326	355.36	0.23	0.66	33
3-methylheptan-1-ol	273–368	362.67	0.9391	376.62	0.69	0.97	33
2-methylheptan-3-ol	273–368	322.58	0.9210	341.56	0.51	1.65	33
3-methylheptan-4-ol	273–368	319.56	0.9138	341.03	0.51	0.88	33
2-methylheptan-5-ol	273–368	343.26	0.9374	357.11	0.56	0.88	33
hexan-1-ol[b,c]	273–368	338.37	0.9345	353.12	0.39	1.18	31
cyclopentanol[b]	273–325	314.91	0.8201	374.45	0.51	1.37	16
Glycols: *P*/MPa, 0–300; *w*, 0.9221; *d*, 0.3754							
1,2-ethanediol	273–368	565.10	0.7070	736.98	0.43	0.78	32
1,2-propanediol	273–368	507.56	0.7399	632.53	0.27	0.66	32
1,3-propanediol	273–368	654.51	0.7579	796.35	1.24	2.21	32
2,2′-oxydiethanol[b]	273–368	528.80	0.6987	697.87	0.24	1.22	32
1,2,3-propanetriol[b,d]	273–368	578.38	0.6528	816.95	0.23	0.50	32
Esters: *P*/MPa, 0–300; *w*, 0.9688; *d*, 0.2910							
glycerol triacetate	273–368	276.88	0.6480	413.97	1.04	1.78	32
glycerol trihexanoate	273–368	360.82	0.7996	437.19	0.83	1.07	32
n-butyl phthalate	273–368	376.53	0.7626	478.34	1.04	1.45	32
methyl oleate	273–368	412.72	0.8947	446.88	0.99	1.30	32
dibenzyl ethylmalonate	273–368	367.45	0.7309	487.08	0.54	0.68	32
Alkyl Halides: *P*/MPa, 0–300; *w*, 0.9712; *d*, 0.2873							
1-chlorobutane	273–368	265.85	0.8150	316.80	0.50	1.25	33
1-chloropentane	273–368	262.28	0.8070	315.66	0.76	1.33	33
1-bromopropane	273–368	164.30	0.5282	302.15	1.28	2.39	33
1-bromobutane	273–368	184.73	0.5656	317.18	0.92	1.63	33
1-bromopentane	273–368	205.97	0.5997	333.54	0.62	1.14	33
iodoethane	293–353	132.30	0.3805	337.69	0.34	0.94	30
1-iodopropane	273–368	162.49	0.4323	365.06	0.74	1.35	33
1-iodobutane	273–368	176.03	0.4676	365.61	0.50	1.28	33
1-iodopentane	273–368	177.45	0.4863	354.39	0.33	0.90	33
chlorobenzene[b,d]	273–368	259.63	0.6833	369.00	0.91	1.71	31
bromobenzene[b,d]	273–368	206.37	0.5133	390.44	0.46	0.87	31

[a] Set of results not taken into account to compute mean values for *d* and *w* for the chemical family to which the substance belongs. [b] Substance or mixture not taken into account to compute mean values for *d* and *w* for its related chemical family. [c] Specific volume data at atmospheric pressure were taken from ref 48. [d] Substance not belonging to the chemical family into which it has been placed for estimation of its volumetric properties, but having the same functional group.

discriminate between the chloro, bromo, or iodo derivatives to get these good results. The results for saturated hydrocarbons are more scattered. While mean errors are generally in the 1% range, maximum errors go up to 3.97% with a mean value of 2% for the family.

The influence of the functional groups seems to predominate because it was possible to predict quite fairly the volumes of chloro- and bromobenzene on one hand and of 1,2,3-propanetriol on the other hand by using mean d and w values corresponding to alkyl halides and glycols, respectively (see Table IV).

Saturated hydrocarbons, alcohols, alkyl halides, esters, and glycols correspond to increasing values of d in this order and to a corresponding decrease of w. Through eq 5, the increase of d is related to the increase of $(\partial p/\partial T)_V$, the slopes of the isochores, and also to the decrease of compressibility as was first observed by Bridgman (*10*). Reduction in compressibility in polar compounds with respect to their nonpolar analogues is thought to be an effect of the ordering role of a polar group on local structure and on molecular packing, as shown by Easteal and Woolf (*27*) and more recently by Uosaki (*47*).

To sum up, an empirical four-parameter equation is given that allows experimental specific volumes of liquids up to 300 MPa to be fit quite correctly at least in the temperature domain ranging approximately from melting to boiling at atmospheric pressure. This equation accounts for the increase of isobaric expansivity and isothermal compressibility when temperature increases. It also predicts a reversal of the sign of internal pressure of the liquids at pressure values at which equilibrium between attractive and repulsive forces is attained; on the contrary, previously proposed similar equations merely contain constant or temperature-dependent only internal pressures. Moreover, in each family of compounds which were studied, it was found that the values of the four parameters involved do not vary much.

Each family of compounds was then characterized by mean values of parameters d and w. These two values, together with two volumes measured at atmospheric pressure, were used to calculate the two other parameters for a given chemical. The ensuing predicted volumes are in good agreement with experimental data up to 300 MPa for alcohols, alkyl halides, esters, and glycols. For saturated hydrocarbons which give the poorest results, the maximum deviation is of the order of 3%.

An equation of state like eq 4 with a small number of parameters, i.e., with a large degree of freedom, may also provide a tool to qualify the coherence of experimental data.

Finally, we think that this four-parameter equation provides a most useful method to get approximate volumes of liquids as a function of pressure when only atmospheric pressure measurements have been performed.

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Glossary

A	dimensionless parameter in eq 2
a	parameter in eqs 4, 5, and 8, >0, dimension: energy
B	parameter in eqs 1–3, dimension: pressure
b	parameter in eqs 1 and 4–8, dimension: volume
C	dimensionless parameter in eq 3
c	parameter in eq 4, >0, dimension: pressure
c	parameter in eq 1, dimension: energy/temperature
d	parameter in eqs 4, 5, 7, and 8, dimension: pression
n	dimensionless parameter in eq 6
p	pressure
s	parameter in eq 6, dimension: pressure × (volume)^n
T	temperature
$(\partial U/\partial V)_T$	internal pressure
V	specific volume
V_0	parameter in eqs 2 and 3, dimension: volume
w	dimensionless combination of parameters of eq 4, $=bc/a$

Greek Letter

ρ	density

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