Equation of State for Saturated Liquids

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An empirical equation, log $(V_f/V_c) = (1 - T_r)^{2/7} \log Z_c$, relates the reduced volume of saturated liquids to the reduced temperature and the critical compressibility factor. This equation holds within experimental uncertainty for 16 diverse substances, including the highly polar ammonia, acetone, and hydrogen cyanide. The equation and the similar equations of Riedel, Yen and Woods, and Bradford and Thodos are compared using 32 sets of liquid-volume data for these 16 substances; this equation is the most precise. Polar substances for which the equation fails—the alcohols, carboxylic acids, and nitriles—are those whose molecules combine into cyclic groups in the liquid state. For conforming substances, with the exception of water, the applicable range is from the triple point to the critical point.

General equations for reduced saturated-liquid density or volume as a function of reduced temperature and critical compressibility factor have been developed (*3, 23, 31*). Herein is presented another such equation (*21*),

$$\log (V_f/V_c) = (1 - T_r)^{2/7} \log Z_c \quad (1)$$

simpler than the other similar equations in that it contains but one right-hand term. The exponent of $(1 - T_r)$ is its only arbitrary component.

Equation 1 becomes an identity at the critical point, $T_r = 1$. As T_r approaches 0, Equation 1 approaches

$$\log (V_0/V_c) = \log Z_c \quad (2)$$

or

$$\rho_0/\rho_c = 1/Z_c \quad (3)$$

Timmermans (*27*) demonstrated that the actual behavior of most liquids is in accord with this relation. He measured the densities of 12 liquids at temperatures between +15° C and their freezing points and fitted cubic equations in temperature to these densities. For all but one of these liquids he found that his equations gave hypothetical liquid densities at absolute zero that satisfy Equation 3. Earlier, van der Waals (*29*) set forth this relation as a general rule, but without verification.

The reduced volumes given by Equation 1 at the two end points, $V_r = 1$ at $T_r = 1$ and $V_r = Z_c$ at $T_r = 0$, are independent of the value of the exponent of $(1 - T_r)$. There is no known theoretical basis for Equation 1 or for the specific value selected for this exponent. The value that most closely reproduces a given set of liquid-volume data generally lies between about 0.275 and 0.295 (*21*). But the uncertainty of these best exponent values is at least ±0.01, owing to the uncertainty of the Z_c values that must be used in their determination. The exponent cannot be made a function of Z_c, because a relation between the exponent and Z_c is not even detectable. The particular value, $^2\!/_7$, that was selected as a universal exponent for all conforming substances lies near the middle of the possible range of a universal value.

The exponential form of Equation 1 can be expanded into its Maclaurin's series,

$$V_f/V_c = Z_c^{+[(1 - T_r)^{2/7}]}$$

$$= 1 + (\ln Z_c)(1 - T_r)^{2/7} + \frac{(\ln Z_c)^2}{2!}(1 - T_r)^{4/7} \quad (4)$$

$$+ \frac{(\ln Z_c)^3}{3!}(1 - T_r)^{6/7} + \ldots \quad (5)$$

or

$$\rho_f/\rho_c = Z_c^{-[(1 - T_r)^{2/7}]} \quad (6)$$

$$= 1 + (-\ln Z_c)(1 - T_r)^{2/7} + \frac{(-\ln Z_c)^2}{2!}(1 - T_r)^{4/7} + \ldots \quad (7)$$

which then more resembles the other correlation equations. The equation of Riedel (*23*) contains two $(1 - T_r)$ terms:

$$\rho_r = 1 + [(1/Z_c - 1.211)/1.3](1 - T_r)^{1/3} + 0.85\,(1 - T_r) \quad (8)$$

The equation of Yen and Woods (*31*) contains three $(1 - T_r)$ terms, the exponents of which are $^1\!/_3$, $^2\!/_3$, and $^4\!/_3$, and the coefficients of which are cubic functions of Z_c. The equation of Bradford and Thodos (*3*) also contains three $(1 - T_r)$ terms. The three coefficients and the smallest of the three exponents are linear functions of Z_c.

A well-known text (*11*) states that the reduced saturated-liquid density table of Lydersen, Greenkorn, and Hougen (*15*) was derived from the data of Riedel (*23*). Riedel's equation replicates the $Z_c = 0.25$, 0.27, and 0.29 columns of this table with minimum standard errors of 0.07, 0.05, and 0.11%, respectively, when $Z_c = 0.2508$, 0.2710, and 0.2955, respectively, are used in this equation.

TESTING AND COMPARISON WITH OTHER EQUATIONS

Equation 1 contains the three parameters T_c, Z_c, and V_c. Substituting Z_cRT_c/P_c for V_c merges the uncertainty of Z_c and V_c,

$$\log V_f = [1 + (1 - T_r)^{2/7}] \log Z_c - \log (P_c/RT_c) \quad (9)$$

In testing the proposed equation and comparing it and the three similar equations cited, each equation was put into a $V_f = V_f(T, T_c, P_c, Z_c)$ form. For each of 16 test substances (Table I or II), a single value of T_c and of P_c (Table II) was used in this testing, but for each substance several values of Z_c were used, as described below.

In the initial test Z_c values taken from five literature sources (*3, 10, 15, 22, 31*) were used. These Z_c values and the standard per cent errors of estimate when these Z_c values are used with each equation are listed in Table I. The uncertainty of recorded Z_c values and the sensitivity of calculated V_f to variations of Z_c are here exemplified. An error listed in Table I is not really a measure of the accuracy of that equation for that substance, but rather is primarily a measure of how close the Z_c value used is to the best-fitting Z_c for that equation and that substance. Because of the uncertainty of Z_c values (or equivalently, of V_c values), the accuracy of the equations cannot be determined.

The precision of any of the equations, however, can be determined by making Z_c a free parameter—that is, using that Z_c value which brings about the best agreement of the equation and a given set of density data. Equation 9 can be rearranged into a form explicit in Z_c,

$$\log Z_c = \frac{\log V_f + \log (P_c/RT_c)}{1 + (1 - T_r)^{2/7}} \qquad (10)$$

For the same 16 substances of the initial test, the mean of the Z_c values given by Equation 10 for each data set and the standard deviation of Z_c from this mean are listed in Table II. These standard deviations are generally less than 0.3%. For each of 12 of the substances two or three sets of data were examined and the results listed separately, so that the agreement or lack of agreement of the mean calculated Z_c values would be shown.

Rather than the mean of the Z_c values given by Equation 10, the Z_c value given by the linear-regression equation,

$$\log Z_c = \frac{\log (P_c/RT_c)\sum[1 + (1 - T_r)^{2/7}] + \sum[1 + (1 - T_r)^{2/7}] \log V_f}{\sum[1 + (1 - T_r)^{2/7}]^2} \qquad (11)$$

was used in the determination of the precision of the proposed equation. This Z_c minimizes the standard error of estimate of log V_f. The Z_c value given by Equation 11, however, is generally almost identical to the mean of those given by Equation 10. Their difference is less than 0.0001 for each of the data sets of Table II.

The standard errors of estimate of ln V_f (equivalent to the standard relative errors of estimate of V_f) when Equation 11 Z_c values are used in Equation 9 are listed in Table II. These standard errors of V_f are generally less than 0.5%. A Z_c value listed in Table II is not implied to be correct, but only to be most consistent with Equation 9, the particular density-data set, and the values of T_c and P_c that were used.

Best Z_c values to be used in the other liquid-density equations were obtained by using equations or methods analogous to Equation 10. The standard errors that were found when these Z_c values are used in these other equations are not listed here, but the largest of the individual V_f errors number as follows. The Bradford-Thodos equation gives 13 errors greater than 2%, but all but one are for substances for which $Z_c < 0.255$. Bradford and Thodos formulated the expressions for their equation coefficients and variable exponent to fit best the observed densities of 12 hydrocarbons, for each of which $Z_c > 0.255$; their equation cannot be extrapolated to substances with lower

Table I. Testing of Saturated-Liquid Volume Equations Using Z_c Values Taken from Literature Sources

Substance	Z_c	Source(s) of Z_c Value	Standard % Error of Estimate of V_f				Source of Liquid Volume Data
			Eq. 9	Riedel eq.	Yen & Woods eq.	Bradford & Thodos eq.	
Neon	0.296	(*22*)	2.81	2.69	2.90	3.34	(*18*)
	0.304	(*15*)	1.58	2.16	1.84	1.09	
Nitrogen	0.288	(*10*)	0.87	0.98	1.30	1.19	(*20*)
	0.291	(*15, 22, 31*)	0.95	1.21	2.35	0.58	
Hydrogen cyanide	0.197	(*15, 22*)	4.99	3.69	24.59	15.02	(*4*)
Water	0.230	(*15, 22, 31*)	0.41	2.77	2.98	1.59	(*1*)
Ammonia	0.242	(*22, 31*)	3.25	4.39	1.39	1.81	(*7*)[a]
	0.243	(*15*)	2.57	3.69	1.02	1.46	
n-Pentane	0.268	(*10*)	0.40	0.61	0.81	0.71	(*32*)
	0.269	(*3, 15, 22, 31*)	0.51	0.51	1.31	0.80	
2-Methylbutane	0.268	(*15, 22*)	0.93	1.21	0.51	0.98	(*32*)
	0.269	(*10*)	0.44	0.67	0.67	0.61	
	0.272	(*31*)	1.44	1.33	2.29	1.49	
Ethylene	0.270	(*15, 22*)	7.02	7.34	6.27	6.97	(*19*)
	0.283	(*10*)	0.48	0.59	1.58	0.29	
	0.284	(*3*)	0.98	1.09	2.08	0.72	
	0.285	(*31*)	1.52	1.65	2.60	1.24	
Acetylene	0.274	(*15, 22, 31*)	0.51	0.53	1.52	0.31	(*17*)
Benzene	0.270	(*3*)	0.62	0.37	1.34	0.93	(*32*)
	0.274	(*15, 22, 31*)	2.98	2.74	3.74	3.07	
Tetrachloromethane	0.272	(*15*)	0.22	0.53	0.59	0.34	(*32*)
Diethyl ether	0.255	(*22*)	5.22	6.02	4.79	4.70	(*32*)
	0.261	(*15*)	1.59	2.16	1.30	1.42	
Acetone	0.237	(*22*)	5.48	7.19	3.11	3.94	(*12*)
	0.238	(*15, 31*)	4.82	6.47	2.65	3.36	
Ethyl acetate	0.252	(*15, 22*)	1.39	2.19	0.68	1.06	(*32*)
Diethylamine	0.270	(*22*)	5.78	5.51	6.34	5.92	(*12*)
	0.286	(*15*)	14.88	15.17	15.36	14.66	
Ethyl mercaptan	0.274	(*15, 22*)	2.28	2.08	3.04	2.30	(*2*)

[a] Data used as presented in (*12*).

Table II. Indirect Testing of Proposed Saturated-Liquid Volume Equation

Substance	Mean Z_c, Eq. 10	Std. Devn., Z_c, $\times 10^4$	Std. Error of Estimate, ln $V_f \times 10^4$	No. of Data Points	T_r Range of Data Used		Source of Liquid Volume Data	T_c, °K	P_c, Atm
Neon	0.3011	4.4	21.8	10	0.567	0.9689	(*18*)	44.4	26.2
Nitrogen	0.2895	8.4	40.9	11	0.513	0.9906	(*20*)	126.2	33.5
	0.2886	4.2	25.4	9	0.496	0.718	(*30*)		
	0.2901	1.5	8.6	15	0.615	0.830	(*26*)		
Hydrogen cyanide	0.1915	0.3	2.7	11	0.569	0.653	(*4*)	456.7	53.2
Water	0.2297	6.1	38.1	21	0.824	0.9910	(*1*)	647.3	218.2
Ammonia	0.2468	5.1	30.7	43	0.479	0.9944	(*7*)[a]	405.4	111.4
	0.2465	4.0	25.4	10	0.550	0.9698	(*13*)		
n-Pentane	0.2684	7.6	35.6	29	0.581	0.9999	(*32*)	470.3	33.3
	0.2685	3.1	21.9	19	0.291	0.613	(*27*)[b]		
	0.2688	1.8	11.7	14	0.478	0.708	(*14*)		
2-Methylbutane	0.2695	6.1	33.0	25	0.593	0.9993	(*32*)	460.9	32.9
	0.2697	5.6	39.0	20	0.250	0.625	(*27*)[b]		
	0.2688	2.4	16.9	20	0.250	0.334	(*8*)		
Ethylene	0.2824	5.5	30.0	15	0.453	0.9941	(*19*)	282.7	50.0
	0.2818	1.1	6.6	8	0.582	0.721	(*16*)		
Acetylene	0.2731	3.4	17.2	12	0.807	0.9885	(*17*)	308.7	61.2
	0.2728	1.0	6.4	9	0.620	0.706	(*16*)		
Benzene	0.2691	4.6	24.1	31	0.486	0.9949	(*32*)	562.1	48.2
	0.2692	1.2	8.2	11	0.522	0.593	(5)		
Tetrachloromethane	0.2722	3.2	17.8	28	0.491	0.9762	(*32*)	556.4	45.0
	0.2723	1.9	12.1	7	0.518	0.626	(*9*)		
Diethyl ether	0.2636	6.0	33.1	23	0.585	0.9980	(*32*)	467.1	35.7
	0.2639	2.5	17.6	19	0.321	0.618	(*27*)[b]		
	0.2639	2.1	14.3	39	0.328	0.735	(*25*)		
Acetone	0.2452	9.8	61.2	19	0.648	0.9895	(*12*)	508.5	46.8
	0.2463	2.4	18.3	12	0.351	0.537	(*27*)[b]		
Ethyl acetate	0.2540	6.7	40.6	28	0.522	0.9980	(*32*)	523.2	37.9
	0.2544	2.4	17.4	13	0.363	0.553	(*27*)[b]		
Diethylamine	0.2604	6.5	35.2	18	0.662	0.9939	(*12*)	496.2	36.2
	0.2602	7.3	46.9	10	0.470	0.833	(*6*)		
Ethyl mercaptan	0.2701	4.9	26.5	19	0.547	0.9845	(2)	499.2	54.2

[a] Data used as presented in (*12*). [b] Data used as presented in (*28*).

Z_c values. The Yen-Woods equation gives 13 errors greater than 1.5%, three of which are greater than 2%. Riedel's equation gives 13 errors greater than 1%, two of which are greater than 1.5%. Equation 9 gives but three errors greater than 1%, and none is greater than 1.5%. Thus, for this group of saturated-liquid-density data sets, the equation here proposed is more precise than any of the others.

CONFORMING LIQUIDS AND NONCONFORMING LIQUIDS

Equation 9 was tested indirectly with the liquid-density data of 106 substances and found to hold within experimental uncertainty for 93. The results of this testing of 16 of the conforming liquids are presented in Table II. The ln (V_f/V_c) *vs.* T_r curves of several of these 16 liquids are shown in Figure 1. Several of the conforming liquids are polar—e.g., hydrogen cyanide, ammonia, and acetone. This correlation fails, however, with certain classes of polar compounds—viz., the alcohols, the carboxylic acids, and the nitriles. (Acetonitrile is that one of Timmermans' 12 liquids that he found did not comply with the Equation 3 relation.) The ln (V_f/V_c) points of a representative of each of these classes are plotted in Figure 2. The curves on which these points would lie intersect the curves predicted by Equation 1. The rapid rate of volume decrease with temperature decrease in the critical region does not belie the very low critical compressibility factors of these three compounds. But then this rapid rate diminishes faster than these low Z_c values and Equation 1 predict.

Saum (*24*) has demonstrated, mainly on the basis of observed viscosities, that molecules of carboxylic acids and of nitriles tend to dimerize in their liquid phases, and that alcohol molecules combine to form larger groups, possibly tetramers. The attraction between the molecules of a cyclic group will be much stronger than the attraction between molecules in different groups. The rapid volume decrease in the critical region for these compounds is brought about by the strong intragroup forces, while the less-than-predicted rate of decrease at lower temperatures is brought about by the weaker intergroup forces. Nitrogen dioxide, whose molecules dimerize, also does not conform. At least one additional parameter would be needed to correlate these departures from predicted behavior.

The correlation also fails for those two liquids that exhibit the largest quantum effects, helium and hydrogen. Water conforms at reduced temperatures above ~0.82 (Table II); it does not conform at lower temperatures. For 11 of the test substances one of the data sets of Table II contains at least one point within 2° of the triple point. Except for water (and deuterium oxide), no conforming substance has been found that does not continue to conform down

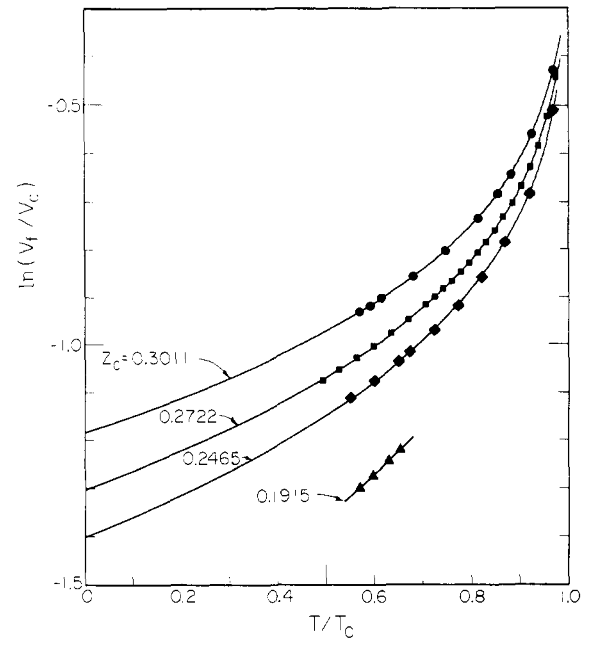

Figure 1. Reduced volume as function of reduced temperature
Liquids that conform
● Neon (*18*)
■ Tetrachloromethane (*32*)
● Ammonia (*13*)
▲ Hydrogen cyanide (*4*)
—Calculated

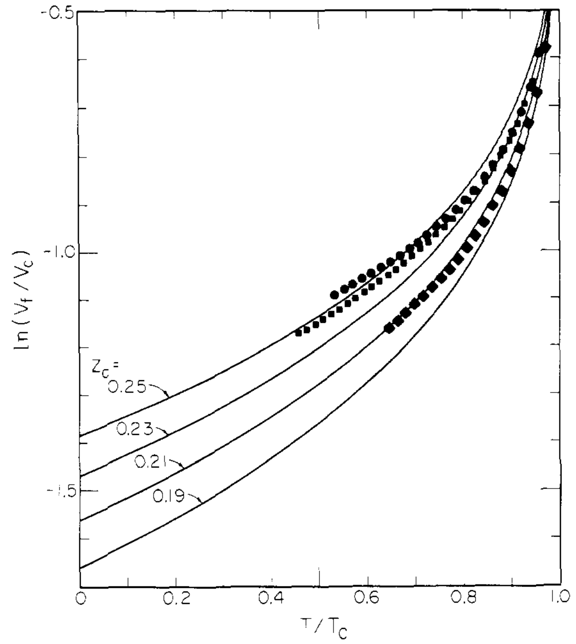

Figure 2. Reduced volume as function of reduced temperature
Polar liquids that do not conform
● Methanol (*32*)
■ Acetic acid (*32*)
▲ Acetonitrile (*12*)
—Calculated

to the lowest temperatures at which the liquid density has been measured. At the other temperature extreme, many of the data sets of Table II demonstrate that the proposed equation is applicable in the critical region.

NOMENCLATURE

ln = natural logarithm of
log = logarithm of: base is optional
P_c = critical pressure
R = gas-law constant
T = temperature: absolute
T_c = critical temperature
T_r = reduced temperature = T/T_c
V_c = critical volume
V_f = saturated-liquid volume
V_r = reduced saturated-liquid volume = V_f/V_c
V_0 = hypothetical saturated-liquid volume at $T_r = 0$
Z_c = critical compressibility factor = V_cP_c/RT_c. Z_c is dimensionless; the units of R must be consistent with those of P_c, T_c, and V_c
ρ_c = critical density
ρ_f = saturated-liquid density
ρ_r = reduced saturated-liquid density = ρ_f/ρ_c
ρ_0 = hypothetical saturated-liquid density at $T_r = 0$

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