

available method. Previously the authors have shown that for predicting the saturated liquid density of pure compounds the Rackett equation is accurate, simple, and versatile (31). The extension of this correlation to mixtures should prove useful in numerous applications.

For the systems of Tables III and IV Harmen's method for predicting bubble-point densities is essentially equivalent in accuracy to Equation 10. In order to maintain this accuracy, however, both Harmen's method and the proposed method require one empirical constant (C for the method of Harmens and Z_{RA} for Equation 10). One contrast in the two methods is the range of compounds for which they can be applied. Whereas Harmens' method was developed mainly for hydrocarbons in the C_1 - C_7 range, the modified Rackett equation has been shown to be reliable for heavier hydrocarbons, organic compounds, and inorganic compounds (31).

Nomenclature

K = correlating parameter of Lu chart
 N = number of data points
 P_c = critical pressure, atm
 P_r = reduced pressure, P/P_c
 R = universal gas constant, 82.06 atm cm³/g mol K
 T = temperature, K
 T_c = critical temperature, K
 T_{cm} = pseudocritical temperature of mixture, K
 T_r = reduced temperature, T/T_{cm}
 V_{bp} = bubble-point volume, cm³/g mol
 V_{cm} = pseudocritical volume of mixture, cm³/g mol
 V_s = volume of saturated liquid, cm³/g mol
 Z_c = critical compressibility factor
 Z_{cm} = critical compressibility factor for mixture
 Z_{RA} = constant of modified Rackett equation

Greek Letters

ρ_{bp} = bubble-point density, g mol/cm³
 ρ_c = critical density, g mol/cm³

ρ_r = reduced density, ρ/ρ_c
 ρ_s = saturated liquid density, g mol/cm³

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Saturated Liquid Molar Volumes. The Rackett Equation

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A slightly modified form of the generalized Rackett equation is presented which improves its predictive accuracy by about an order of magnitude.

Rackett (7) recently proposed an unusually simple generalized equation for predicting liquid volumes. The accuracy of this equation, however, is only moderate. Spencer and Danner (9) found average deviations of 2.40% between calculated and experimental liquid volumes. These latter investigators have also modified this equation to predict liquid volumes with high accuracy, but the modified relationship is no longer entirely generalized because it requires one curve fitted constant for each pure compound. A generalized form of the Rackett equation is proposed here which is also very accurate.

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$$V = V_{scr} Z_{cr}^{(1-T'_R)^{2/7}} \quad (1)$$

where

$$Z_{cr} = 0.29056 - 0.08775 \omega$$

and where V_{scr} is defined as

$$V_{scr} = V' \exp \left[-(1 - T'_R)^{2/7} \ln (0.29056 - 0.08775 \omega) \right] \quad (2)$$

The original Rackett equation used the critical volume and the critical compressibility factor as parameters. Both are subject to large experimental errors which hamper seriously the predictive accuracy of the Rackett equation. The proposed relationship circumvents these problems.

One liquid density is required to calculate the scaling volume, V_{scr} , but this is not a shortcoming for a generalized relationship. For every compound for which critical volumes have been determined liquid molar volumes are

similarly available. For a number of compounds, however, the critical temperature and at least one liquid density have been measured experimentally, but not the critical volume.

In calculating the scaling volume, T'_R should be chosen in a region in which liquid density is known with the greatest accuracy. This temperature will often be at the normal boiling point or in the range of 20–25°C. Frequently, there will be a number of measurements by different investigators at these temperatures, and the absolute accuracy of these measurements can be estimated. These considerations are important because the predictive capability of Equation 1 is directly proportional to the accuracy of V_{scr} . If high precision data are available over a wide range of temperature, a least squares fitting procedure may be used to calculate V_{scr} ; and this has been done in the present case. For this purpose the tabulation of critical constants by Kudchadker et al. (4) has been used for critical temperatures. Because Equation 1 is very accurate, the value of V_{scr} must be consistent with T_c . Thus each time new recommended values for the critical temperature are compiled, new values for V_{scr} must also be calculated from Equation 2.

Equation 1 has been tested with the identical data set employed by the authors in a previous investigation (2). For 26 nonpolar compounds the average absolute deviation

between calculated and experimental liquid volumes is 0.286%. This compares with an average deviation of 0.206% for the same data set for the correlation presented previously (2). Table I shows the comparison for the individual compounds. To test the two correlations on a comparable basis, identical fitting procedures were adopted. Optimized values of V_{scr} were used in Equation 1; and, therefore, optimized V_{sc} values were used in the correlation of Gunn and Yamada (2). This optimization reduced the average deviation from 0.22% reported in the original reference to 0.206% reported here. Obviously, the V_{sc} values employed here are slightly different than those originally reported and both sets are slightly different than the V_{scr} values. It is emphasized, however, that the variations between all three sets of V_{sc} are considerably less than that normally encountered between experimental critical volume measurements by different investigators.

This investigation shows that the correlation of Gunn and Yamada (2) has average deviations about 25% lower than Equation 1. This conclusion may be misleading, however, because both correlations probably are within experimental accuracy. The absolute difference in deviations for the two correlations is only 0.08%, and there is considerable question as to how meaningful this difference is. Even for a compound as widely studied as

Table I. Deviations Between Calculated and Experimental Saturated Liquid Volumes

Compound	Reduced temp. range, °C	No. of data points	Vol % deviation				V_{scr} , cc/mol	Data source
			Gunn-Yamada (2)		This work Eq. 1			
			Av.	Max.	Av.	Max.		
Argon	0.56 to 1.0	27	0.32	1.40	0.73	2.81	75.74	(1, 5)
Nitrogen	0.50 to 0.95	14	0.20	0.56	0.18	0.37	89.95	(1)
Carbon monoxide	0.51 to 1.0	26	0.38	1.08	0.35	0.88	91.94	(1)
Carbon dioxide	0.86 to 1.0	9	0.33	1.07	0.40	2.34	93.78	(1)
Methane	0.47 to 0.97	20	0.40	1.77	0.33	0.88	99.53	(1)
Propane	0.22 to 0.99	40	0.18	0.60	0.24	0.90	199.53	(1)
Isobutane	0.74 to 0.98	5	0.43	0.65	0.41	0.72	256.44	(10)
<i>n</i> -Pentane	0.291 to 1.0	55	0.18	1.03	0.27	0.86	310.87	(8, 10, 12)
<i>n</i> -Hexane	0.56 to 0.95	21	0.17	0.37	0.32	0.71	367.50	(12)
2,3-Dimethylbutane	0.55 to 0.97	22	0.34	0.66	0.45	1.01	359.26	(12)
<i>n</i> -Heptane	0.34 to 0.99	65	0.17	0.81	0.31	1.04	429.08	(8, 12)
2,2,3-Trimethylbutane	0.53 to 0.57	3	0.02	0.02	0.01	0.02	412.97	(8)
<i>n</i> -Octane	0.48 to 0.94	27	0.18	0.64	0.44	0.77	490.22	(12)
Cyclohexane	0.52 to 0.68	8	0.16	0.40	0.15	0.27	309.42	(10)
Ethylene	0.45 to 0.99	14	0.38	1.91	0.38	2.44	130.77	(10)
Benzene	0.49 to 0.99	30	0.24	0.69	0.18	0.86	255.92	(12)
Toluene	0.56 to 0.67	4	0.04	0.06	0.03	0.05	314.53	(10)
<i>o</i> -Xylene	0.54 to 0.61	5	0.05	0.07	0.06	0.10	367.58	(8)
Ethylbenzene	0.29 to 0.65	26	0.09	0.33	0.29	0.62	369.34	(8, 10)
Chlorobenzene	0.36 to 0.86	34	0.08	0.42	0.17	0.30	305.38	(10, 12)
Bromobenzene	0.56 to 0.81	18	0.09	0.35	0.11	0.22	320.47	(12)
Methanol ^a	0.53 to 0.98	24	1.92	3.84	2.67	6.20	118.36	(12)
Ethanol ^a	0.53 to 0.99	25	1.81	4.24	2.68	5.49	173.55	(12)
1-Propanol ^a	0.66 to 0.99	19	0.71	1.90	1.37	3.26	224.24	(12)
Ethyl ether	0.32 to 0.99	37	0.10	0.47	0.21	0.53	281.27	(10)
Acetic acid ^a	0.46 to 0.98	34	0.67	1.42	1.11	2.16	175.77	(10)
Methyl formate ^a	0.56 to 0.99	22	0.39	1.21	0.30	1.70	169.92	(12)
Ethyl acetate	0.36 to 0.98	36	0.22	1.31	0.20	0.49	284.35	(10)
Methyl butyrate	0.56 to 0.99	25	0.21	0.65	0.28	0.47	338.65	(12)
Acetone	0.56 to 0.64	5	0.06	0.11	0.03	0.07	208.40	(10)
Acetonitrile ^a	0.89 to 0.98	6	2.80	4.53	2.52	4.37	159.24	(10)
Ethyl mercaptan	0.55 to 0.99	16	0.32	0.75	0.19	0.43	202.28	(10)
Grand av. dev.		592	0.206	0.75	0.286	0.86		

^aPolar components not included in over-all average deviation. Critical temperatures taken from Kudchadker et al. (4). Critical temperatures used for argon and nitrogen are 150.72 and 126.2K, respectively (3).

argon, the highly regarded experimental report of Michels et al. (5) gives a saturated liquid molar volume of 37.49 at 130.03K. The compilation of argon data by Din (1) recommends a value of 37.20 at the same conditions. This represents a variation of 0.77% in experimental measurements for argon.

Spencer and Danner (9) report an average deviation of 0.38% for their nongeneralized modification of the Rackett equation. This result is not comparable to that given here, because these authors used a different and more complete data set. Experimental error is probably higher also in their data set than in the carefully selected and limited data used here.

High accuracy is achieved with the Rackett equation primarily through the use of the scaling volume. V_{sc} is based on a liquid density which is usually known to within 0.25%. Critical volumes are frequently in error by several percent, and even the group RT_c/P_c will frequently vary 1 to 2% between different experimental investigators, primarily because of the variability in the critical pressure measurements.

Compared with a nongeneralized equation, a generalized relationship such as Equation 1 has three advantages. The only parameters required, T_c , ω , and V_{scr} , are those used to predict any of the configurational thermodynamic properties; and no additional parameter is required specifically to calculate liquid volumes. The scaling volume, defined by Equation 2, is more accurate than the critical volume for predicting both liquid phase and gas phase properties (11). If for a particular compound the critical constants are unknown, then accurate density measurements in conjunction with Equation 1 may be used to make good estimates of the critical parameters (2).

Finally, various correlations for the critical compressibility factor are compared:

$$\text{[From Equation 1]} \quad Z_c = 0.29056 - 0.08775 \omega \quad (3)$$

$$\text{[Gunn and Yamada (2)]} \quad Z_c = 0.2920 - 0.0967 \omega \quad (4)$$

$$\text{[Pitzer et al. (6)]} \quad Z_c = 0.291 - 0.08 \omega \quad (5)$$

Because of the large experimental errors in reported values of Z_c , it does not appear possible at this time to

determine which of the three equations above is more accurate.

The results of this investigation indicate that the correlation of Gunn and Yamada (2) is more accurate than Equation 1, a modified Rackett equation, for predicting saturated liquid volumes. The difference is small, however. Equation 1 is very simple and, therefore, highly recommended.

Nomenclature

R = gas constant

P_c = critical pressure

T_c = critical temperature

T_R = reduced temperature, T/T_c

T'_R = reduced temperature in region of maximum accuracy for liquid density measurements

V = liquid molar volume

V' = experimental liquid molar volume used to define V_{scr} (measured at T'_R)

V_{sc} = scaling volume, defined by Gunn and Yamada (2)

V_{scr} = scaling volume, defined by Equation 2

Z_c = critical compressibility factor

Z_{cr} = critical compressibility factor for the Rackett equation

ω = acentric factor, defined by Pitzer et al. (6)

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