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Prediction of Saturated-Liquid Densities and Critical Volumes for Polar and Nonpolar Substances

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The parameter Z_{RA}, advanced by Spencer and Danner for the calculation of saturated-liquid densities through the relationship $\rho = MP_c/(RT_cZ_{RA}{}^{1+(1-T_R)^{2/7}})$, has been found to vary with temperature over the complete range between the triple point and the critical point. This dependence has been accounted for by replacing Z_{RA} by the temperature-dependent function $\alpha + \beta(1 - T_R)$, where α and β are constants unique to a substance. Data for 62 substances have been used to develop relationships for α and β which predict saturated-liquid densities for quantum, nonpolar, polar, and associated polar liquids with an overall average deviation of 1.32% (4942 points). Nine additional polar and nonpolar compounds were employed to test the reliability of this method. When applied at the critical point, this development defines the critical volume as $v_c = \alpha RT_c/P_c$. Calculated critical volumes yielded an average deviation of 2.14% (68 substances), when compared to actual values available in the literature.

The prediction of densities for the saturated-liquid state continues to play an important role in the calculation of thermodynamic properties. Watson (*1*) in 1943 was the first to attempt a generalization of the density behavior for the liquid state by introducing the ω factor through the relationship

$$\rho = (MP_c/T_c)\omega \tag{1}$$

where $\omega = P_R/(zRT_R)$. For this development, Watson utilizes the *PVT* behavior of isopentane and presents a graphical relationship for this factor against T_R for different parameters of P_R. Unfortunately, this factor is not a truly generalized function of P_R and T_R since it can vary by as much as 20% between different compounds existing at identical reduced conditions. In order to predict density more accurately, Watson suggests the use of a single actual density ρ_1 so that the ratio

$$\rho/\omega = \rho_1/\omega_1 \tag{2}$$

applies. In eq 2, the factor ω_1 corresponds to the pressure and temperature conditions associated with ρ_1.

In 1954, Riedel (*2*) considered only the saturated-liquid state and proposed the generalized relationship

$$\rho_R = 1 + 0.85(1 - T_R) + (0.53 + 0.2\alpha_c)(1 - T_R)^{1/3} \tag{3}$$

where ρ_R is the reduced density and the Riedel factor $\alpha_c = (\mathrm{d}\ \ln P_R/\mathrm{d}\ \ln T_R)_{T_R=1.00}$. Replacement of α_c through the relationship $\omega = 0.203(\alpha_c - 7.90) + 0.242$, given by Sherwood and Reid (*3*), transforms eq 3 to the expression

$$\rho_R = 1 + 0.85(1 - T_R) + (1.6916 + 0.9846\omega)(1 - T_R)^{1/3} \tag{4}$$

where the acentric factor $\omega = -\log P_R|_{T_R=0.700} - 1.000$. Riedel's method expressed through eq 3 and 4 is claimed to predict reliable density values for both nonpolar and polar substances, *but fails to accommodate polar associating liquids*. To extend the method of Riedel to include polar associating liquids, Joffe and Zudkevitch (*4*) replace the factor ω in eq 4 with the temperature-dependent function, ψ, to express reduced density as follows:

$$\rho_R = 1 + 0.85(1 - T_R) + (1.6916 + 0.9846\psi)(1 - T_R)^{1/3} \tag{5}$$

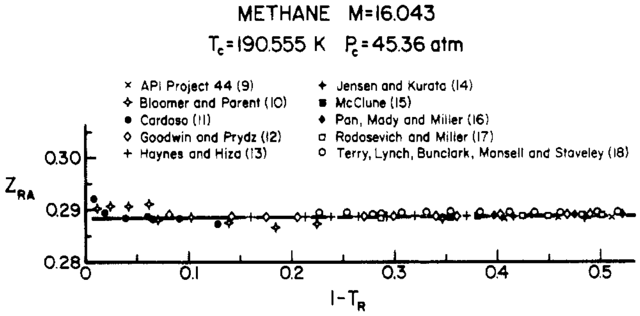

Figure 1. Relationship between Z_{RA} vs. $1 - T_R$ for methane.

For nonpolar compounds, Joffe and Zudkevitch (*4*) propose that ψ is temperature independent and can thus be obtained from a single actual density value. However, for polar compounds ψ was proposed to be linearly dependent on temperature, thus requiring two experimental densities for its establishment.

Yen and Woods (*5*) present another generalized approach for the calculation of saturated-liquid densities based on the critical compressibility factor. For nonpolar and polar liquids, they propose the relationship

$$\rho_R = 1 + A(1 - T_R)^{1/3} + B(1 - T_R)^{2/3} + D(1 - T_R)^{4/3} \tag{6}$$

where the coefficients A, B, and D are polynomials in z_c. On the basis of 62 pure compounds whose z_c values range from 0.21 to 0.29, Yen and Woods calculate densities using eq 6 and compare them with corresponding experimental values to obtain an overall average deviation of 2.1% (693 points).

The critical compressibility factor, z_c, is also used by Rackett (*6*) as a correlating parameter to define reduced density for saturated liquids as

$$\rho_R = 1/[z_c{}^{(1-T_R)^{2/7}}] \tag{7}$$

Equation 7 is claimed by Rackett to hold for polar and nonpolar substances, but fails for quantum and polar associating liquids. In this context, Rackett suggests that better accuracy could be realized if z_c were made a free parameter chosen to best represent experimental data.

Spencer and Danner (*7*) utilize the suggestion of Rackett and replace z_c by Z_{RA} to define the saturated-liquid density as

$$\rho = \frac{MP_c}{RT_c}\,\frac{1}{Z_{RA}{}^{1+(1-T_R)^{2/7}}} \tag{8}$$

In eq 8, Z_{RA} is a constant specific to a substance and is determined from the linear regression analysis of experimental data representing the saturated-liquid state. The form of eq 8 does not utilize critical density, but requires knowledge of the critical temperature and the critical pressure. Spencer and Danner (*7*) present values of Z_{RA} for 111 polar and nonpolar

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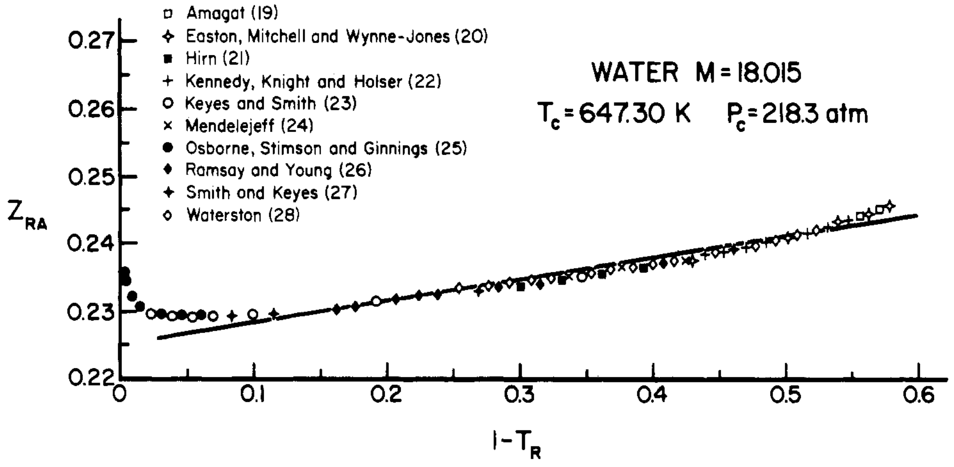

Figure 2. Dependence of Z_{RA} upon $1 - T_R$ for water.

substances. Spencer and Adler (*8*) update and extend this initial study to a total of 165 polar and nonpolar liquids. In this latter study, Spencer and Adler report low deviations for polar and nonpolar compounds, but claim higher deviations for polar associating liquids. For these substances, either the functional form of eq 8 is not proper, or Z_{RA} is not constant. Since the functional form of eq 8 is simple, it was thought best to explore the possibility that Z_{RA} depends on temperature.

Dependence of Z_{RA} on Temperature

Experimental measurements reported in the literature for 62 substances have been utilized to calculate values of Z_{RA} for corresponding values of T_R. This approach entailed the involvement of eq 8 in the form

$$Z_{RA} = [MP_c/(R\rho T_c)]^{1/[1+(1-T_R)^{2/7}]} \qquad (9)$$

Figure 1 presents the results for methane based on the available experimental density measurements of 10 investigators. This figure shows that Z_{RA} for methane is essentially independent of temperature, consistent with the claim of Spencer and Danner (*7*). For water, the available density measurements of 10 investigators have been utilized to develop Figure 2. In this case, Z_{RA} is neither temperature independent nor linearly dependent on $1 - T_R$, but shows a complex behavior which is accentuated in the vicinity of the critical point. Nonetheless, in the present treatment, this behavior was approximated by making Z_{RA} a linear function of $1 - T_R$. Figure 3 presents the Z_{RA} vs. $1 - T_R$ behavior for the quantum liquid helium. This dependence is essentially linear over the complete temperature range, except for the region near the critical point. In this region, the behavior for helium is opposite to that encountered for water. As in the case for water, the overall dependence of Z_{RA} on $1 - T_R$ was assumed to be linear.

The general pattern exhibited in these three figures suggests that, without much loss in accuracy, the adjustable parameter Z_{RA} can be expressed as a linear function of $1 - T_R$ as follows:

$$Z_{RA} = \alpha + \beta(1 - T_R) \qquad (10)$$

A linear regression analysis was applied to experimental densities for 62 substances which included nonpolar, polar, quantum, and polar associating liquids. The results of this analysis expressed as parameters α and β are presented in Table I. These actual parameters give rise to an overall average density deviation of 0.32% (4942 points), when compared with actual values. The maximum deviation was exhibited by xenon, 0.97% (67 points). It should be noted that the actual values of β for nonpolar substances are generally lower than the corresponding values found for quantum and polar liquids. The actual values of α and β resulting from this regression analysis may now be utilized to structure a method for their prediction so that these parameters can be estimated for substances other than those included in this study.

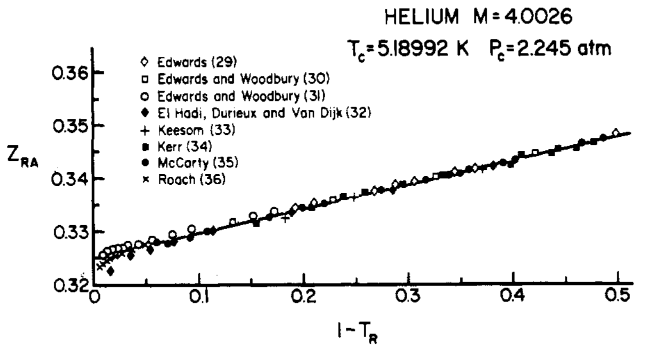

Figure 3. Linear relationship of Z_{RA} vs. $1 - T_R$ resulting from experimental density values for the quantum liquid, helium.

Correlation for Parameter α

Parameter α represents the value of Z_{RA} at the critical point and is numerically much larger than the corresponding slope β. Therefore, the accurate establishment of this parameter becomes essential to the prediction of saturated-liquid densities.

Nonpolar Substances. Several attempts to relate parameter α for nonpolar substances to easily accessible physical properties were made. Of these, the most suitable approach resulted when α was related to the factor s, defined as

$$s = T_{Rb} \ln P_c/(1 - T_{Rb}) \qquad (11)$$

where $T_{Rb} = T_b/T_c$ and P_c is the critical pressure in atmospheres. This factor represents the negative slope of a straight line joining the critical point and the normal boiling point on a $\ln P_R$ vs. $1/T_R$ coordinate system. This method of correlation showed that α for nonpolar substances is linearly dependent on s as follows:

$$\alpha = 0.3883 - 0.0179s \qquad (12)$$

In addition to nonpolar substances, eq 12 also accommodates the behavior of the quantum liquids helium, hydrogen, and neon.

Polar Substances. The presence of an asymmetric charge distribution associated with polar liquids requires that a modification be introduced to eq 12 in order to include the contributions due to this effect. In this regard, the dipole moment,

Table I. Basic Physical Constants, Density Parameters, and Sources of Data for Substances Used To Develop the Method of This Study

substance	M	T_b, K	T_c, K	P_c, atm	μ, D	s	Λ	$10^3\Theta$	T_{Rb}	points	actual			predicted			ref
											α	β	density dev, %	α	β	density dev, %	
monatomic																	
helium	4.0026	4.25	5.18992	2.245	0	3.6567	0.1659	0	0.8189	164	0.3250	0.0458	0.18	0.3228	0.0458	1.02	*29-36*
neon	20.183	27.07	44.417	26.19	0	5.0956	0.0280	0	0.6094	58	0.3009	0.0000	0.32	0.2971	0.0001	2.21	*37-41*
argon	39.948	87.28	150.65	48.02	0	5.3324	0.0088	0	0.5794	128	0.2928	−0.0032	0.21	0.2928	−0.0031	0.22	*16, 18, 42-51*
krypton	83.8	119.92	209.40	54.148	0	5.3497	0.0048	0	0.5727	81	0.2896	−0.0001	0.39	0.2925	−0.0036	1.04	*18, 52-55*
xenon	131.30	165.0	289.74	57.636	0	5.3626	0.0030	0	0.5695	67	0.2897	−0.0055	0.97	0.2923	−0.0038	2.65	*18, 56-59*
diatomic																	
n-hydrogen	2.0157	20.39	33.19	12.80	0	4.0612	0.0890	0	0.6143	54	0.3133	0.0155	0.29	0.3156	0.0157	1.28	*41, 60-64*
p-hydrogen	2.0157	20.268	32.985	12.759	0	4.0581	0.0894	0	0.6145	49	0.3132	0.0176	0.32	0.3157	0.0158	0.96	*64, 65*
nitrogen	28.013	77.35	126.15	33.5	0	5.5659	0.0108	0	0.6132	111	0.2907	−0.0034	0.32	0.2887	−0.0020	1.06	*17, 18, 42, 43, 51, 60, 66-70*
oxygen	31.999	90.18	154.580	49.77	0	5.4716	0.0097	0	0.5834	158	0.2904	−0.0027	0.41	0.2904	−0.0025	0.41	*18, 48, 66, 71-75*
carbon monoxide	28.010	81.65	132.91	34.508	0.112	5.6406	0.0105	0.025	0.6143	45	0.2912	−0.0061	0.31	0.2873	−0.0018	1.70	*18, 43, 76*
fluorine	37.997	85.02	144.31	51.47	0	5.6513	0.0096	0	0.5891	103	0.2891	−0.0024	0.22	0.2871	−0.0020	1.15	*77-80*
chlorine	70.906	239.19	417.15	76.1	0	5.8226	0.0033	0	0.5734	106	0.2780	−0.0028	0.20	0.2841	−0.0023	3.71	*71, 81-84*
hydrogen chloride	36.461	188.0	324.7	82.0	1.08	6.0604	0.0058	0.907	0.5790	53	0.2652	0.0010	0.34	0.2737	−0.0007	4.81	*71, 85-88*
polyatomic																	
carbon dioxide	44.010	185.1	304.19	72.85	0	6.6654	0.0054	0	0.6085	89	0.2747	−0.0118	0.56	0.2690	0.0006	2.80	*89-94*
carbon disulfide	76.13	319	552	78.0	0	5.9648	0.0026	0	0.5779	26	0.2886	−0.0074	0.04	0.2815	−0.0019	2.77	*95-99*
hydrogen sulfide	34.08	213.5	373.15	88.2	0.97	5.9906	0.0055	0.596	0.5722	38	0.2836	−0.0132	0.52	0.2789	−0.0014	1.63	*87, 100, 101*
nitrous oxide	44.013	184.67	309.584	71.596	0.167	6.3142	0.0053	0.021	0.5965	27	0.2761	−0.0027	0.59	0.2753	−0.0005	0.77	*102, 103*
sulfur dioxide	64.059	263.2	430.8	77.81	1.63	6.8380	0.0034	1.114	0.6110	56	0.2661	−0.0011	0.37	0.2559	0.0020	6.34	*104-106*
ammonia	17.030	239.82	405.45	111.7	1.47	6.8282	0.0078	1.468	0.5915	127	0.2463	0.0027	0.15	0.2467	0.0041	0.61	*98, 105, 107-110*
water	18.015	373.15	647.30	218.3	1.85	7.3308	0.0064	1.783	0.5765	148	0.2251	0.0321	0.91	0.2252	0.0328	0.99	*19-28*
aliphatic hydrocarbons																	
methane	16.043	111.63	190.555	45.36	0	5.3953	0.0112	0	0.5858	104	0.2884	0.0016	0.24	0.2917	−0.0025	1.07	*9-18*
ethylene	28.054	169.38	282.35	49.76	0	5.8582	0.0063	0	0.5999	64	0.2824	−0.0028	0.27	0.2834	−0.0018	0.87	*45, 111-115*
ethane	30.070	184.55	305.33	48.16	0	5.9202	0.0056	0	0.6044	89	0.2814	−0.0016	0.31	0.2823	−0.0017	0.58	*9, 13-15, 17, 113, 116-118*
propylene	42.08	225.46	364.8	45.5	0.366	6.1773	0.0040	0.046	0.6180	55	0.2786	−0.0036	0.38	0.2777	−0.0011	0.54	*113, 119-122*
propane	44.09	231.05	369.85	41.916	0.084	6.2185	0.0038	0.002	0.6247	152	0.2758	0.0005	0.43	0.2770	−0.0010	0.42	*9, 13-15, 17, 113, 118, 120, 123-126*
2-methylpropane	58.12	261.45	408.13	36.00	0.132	6.3874	0.0029	0.004	0.6406	116	0.2756	−0.0012	0.17	0.2740	−0.0006	0.87	*13, 15, 118, 120, 127-131*
n-butane	58.12	272.65	425.4	37.47	0	6.4678	0.0028	0	0.6409	84	0.2726	0.0003	0.31	0.2725	−0.0003	0.38	*9, 13, 15, 118, 120, 132, 133*
2-methylbutane	72.15	301.03	460.39	33.37	0.13	6.6259	0.0023	0.003	0.6539	95	0.2723	−0.0008	0.29	0.2697	0.0001	1.41	*15, 129, 134-137*
n-pentane	72.15	309.21	469.77	33.25	0	6.7482	0.0022	0	0.6582	99	0.2682	0.0006	0.22	0.2675	0.0005	0.50	*9, 15, 120, 134, 135, 138-140*
n-hexane	86.18	341.88	507.9	29.73	0	6.9854	0.0019	0	0.6731	86	0.2625	0.0033	0.20	0.2633	0.0012	0.24	*9, 134, 138, 141-146*
n-heptane	100.21	371.58	540.6	27.00	0	7.2457	0.0016	0	0.6873	126	0.2603	0.0012	0.31	0.2586	0.0020	0.96	*9, 134, 138, 142-144, 147-153*
n-octane	114.23	398.82	568.83	24.54	0	7.5075	0.0014	0	0.7011	69	0.2559	0.0030	0.21	0.2539	0.0029	1.43	*9, 134, 137, 138, 142-144*
naphthenes																	
cyclopropane	42.08	240.34	398.31	55.065	0	6.0987	0.0040	0	0.6034	25	0.2750	−0.0041	0.41	0.2791	−0.0014	2.08	*154*
cyclohexane	84.16	353.88	553.45	40.2	0	6.5500	0.0019	0	0.6394	95	0.2728	0.0002	0.16	0.2711	−0.0001	1.21	*136, 137, 141, 142, 155-161*

methylcyclohexane	98.19	374.08	572.12	34.26	0	6.6754	0.0017	0	0.6538	59	0.2687	0.0031	0.21	0.2688	0.0002	0.70	*136, 142, 148, 155, 157, 162*
aromatics																	
benzene	78.11	353.24	562.16	48.34	0	6.5573	0.0021	0	0.6284	202	0.2697	−0.0003	0.20	0.2709	−0.0001	0.79	*99, 121, 136, 137, 142, 157, 163–172*
toluene	92.14	383.78	591.79	40.50	0.36	6.8289	0.0018	0.015	0.6485	125	0.2645	−0.0003	0.26	0.2661	0.0007	1.32	*99, 135, 136, 157, 158, 162, 166, 169, 170, 173, 174*
o-xylene	106.17	417.58	630.3	36.81	0.62	7.0783	0.0015	0.036	0.6625	103	0.2615	0.0024	0.21	0.2616	0.0015	0.29	*142, 157, 162, 166, 169, 170, 175–178*
m-xylene	106.17	412.27	617.05	34.89	0.34	7.1514	0.0015	0.011	0.6681	105	0.2573	0.0047	0.13	0.2603	0.0017	1.19	*99, 142, 157, 162, 166, 169, 170, 175, 177–179*
p-xylene	106.17	411.52	612.2	34.65	0	7.1280	0.0015	0	0.6678	83	0.2581	0.0026	0.11	0.2607	0.0017	1.46	*136, 142, 157, 162, 166, 169, 170, 175, 177, 178*
alcohols																	
methanol	32.04	337.70	512.58	79.91	1.70	8.4597	0.0042	0.879	0.6588	102	0.2273	0.0219	0.65	0.2282	0.0228	0.93	*99, 135, 180–186*
ethanol	46.07	351.44	516.25	62.96	1.69	8.8334	0.0032	0.675	0.6808	78	0.2437	0.0244	0.31	0.2474	0.0205	1.44	*99, 137, 180, 181, 184, 185, 187, 188*
2-propanol	60.10	355.39	508.3	47.00	1.66	8.9484	0.0026	0.501	0.6992	45	0.2447	0.0182	0.48	0.2592	0.0179	8.61	*181, 185, 189, 190*
1-propanol	60.10	370.30	536.71	51.02	1.68	8.7501	0.0025	0.500	0.6899	74	0.2476	0.0189	0.60	0.2511	0.0173	1.91	*137, 171, 181, 184, 185, 189, 191*
2-methyl-1-propanol	74.12	381.15	547.78	42.44	1.64	8.5734	0.0021	0.380	0.6958	48	0.2518	0.0145	0.52	0.2514	0.0146	0.60	*182, 185, 189, 192, 193*
2-butanol	74.12	372.66	536.05	41.24	1.65	8.4832	0.0021	0.391	0.6952	53	0.2495	0.0141	0.40	0.2496	0.0145	0.42	*158, 181, 189, 193*
2-methyl-2-propanol	74.12	355.7	506.21	39.21	1.66	8.6708	0.0022	0.422	0.7027	19	0.2539	0.0068	0.36	0.2565	0.0156	2.95	*189, 192, 193*
1-butanol	74.12	390.88	563.05	43.65	1.66	8.5732	0.0021	0.379	0.6942	95	0.2517	0.0144	0.28	0.2505	0.0145	0.77	*171, 180, 181, 184, 185, 189, 190, 192, 193*
1-pentanol	88.15	411.13	588.15	38.58	1.66	8.4835	0.0018	0.307	0.6990	63	0.2557	0.0094	0.40	0.2517	0.0129	1.98	*180, 181, 184, 185, 192, 194, 195*
1-octanol	130.23	468.31	652.5	28.2	1.62	8.4904	0.0012	0.174	0.7177	63	0.2563	0.0059	0.27	0.2614	0.0103	4.44	*156, 180, 181, 184, 185, 192, 194*
miscellaneous																	
methyl chloride	50.49	249.06	416.27	65.919	1.87	6.2387	0.0037	1.330	0.5983	50	0.2686	−0.0025	0.74	0.2613	0.0009	4.40	*167, 196–199*
carbon tetrachloride	153.82	349.9	556.3	44.98	0	6.4525	0.0015	0	0.6290	137	0.2720	0.0005	0.16	0.2728	−0.0005	0.29	*99, 136, 167, 168, 170, 200–204*
ethyl acetate	88.11	350.30	523.2	37.8	1.78	7.3592	0.0019	0.438	0.6695	64	0.2529	0.0027	0.22	0.2555	0.0025	1.64	*99, 135, 137, 205, 206*
diethyl ether	74.12	307.58	466.74	35.90	1.15	6.9198	0.0023	0.218	0.6590	77	0.2636	0.0027	0.25	0.2642	0.0011	0.25	*97, 99, 135, 137, 182, 207*
diethylamine	73.14	329.05	496.6	36.6	0.92	7.0701	0.0022	0.126	0.6626	18	0.2605	0.0045	0.29	0.2617	0.0016	0.31	*208, 209*

Table I (*Continued*)

											actual			predicted			
substance	M	T_b, K	T_c, K	P_c, atm	μ, D	s	Λ	$10^3\Theta$	T_{Rb}	points	α	β	density dev, %	α	β	density dev, %	ref
pyridine	79.10	388.41	620.0	55.6	2.19	6.7391	0.0020	0.694	0.6265	28	0.2683	−0.0055	0.05	0.2645	0.0007	0.42	*135, 210*
acetonitrile	41.05	354.72	547.85	47.7	3.92	7.0987	0.0030	2.442	0.6475	47	0.1951	0.0130	0.36	0.1951	0.0161	0.91	*135, 211–213*
propionitrile	55.08	370.29	564.4	41.3	4.02	7.0980	0.0024	2.095	0.6561	32	0.2116	0.0125	0.48	0.2155	0.0103	2.66	*213–215*
acetone	58.08	329.35	508.10	46.39	2.88	7.0699	0.0026	1.490	0.6482	78	0.2429	0.0046	0.37	0.2416	0.0043	0.99	*135, 163, 172, 186, 216–219*
acetic acid	60.05	391.05	592.71	57.10	1.74	7.8435	0.0024	0.492	0.6598	51	0.2165	0.0226	0.42	0.2184	0.0142	1.29	*99, 137, 185, 201, 220, 221*
chlorobenzene	112.56	404.87	632.4	44.6	1.69	6.7577	0.0015	0.319	0.6402	73	0.2644	0.0019	0.16	0.2668	0.0005	1.25	*99, 135–137, 168, 222*
dimethyl sulfide	62.13	310.48	503.0	54.6	1.50	6.4509	0.0027	0.486	0.6173	23	0.2658	0.0085	0.35	0.2715	−0.0003	2.49	*223*
										4942			0.32 (av)			1.32 (av)	

μ, of the substance has been used to define the reduced dipole moment

$$\Theta = P_c\mu^2/T_c^2 \qquad (13)$$

where μ is expressed in debye units, P_c in atmospheres, and T_c in K. The introduction of this parameter extends the application of eq 12 to polar compounds through the relationship

$$\alpha = 0.3883 - 0.0179s - 130540\Theta^{2.41} \qquad (14)$$

Equation 14 satisfactorily predicts values of α for polar substances with the exception of water, alcohols, and carboxylic acids. For these associating polar liquids that contain a hydroxyl group, an extension of eq 14 does not prove adequate and therefore the correlation of α for this class of compounds requires a separate treatment.

Polar Compounds Containing a Hydroxyl Group. For compounds containing a hydroxyl group, α is strongly influenced by T_{Rb}, the reduced normal boiling point. With the additional introduction of the critical pressure, the prediction of parameter α, for this class of compounds, becomes

$$\alpha = \left[0.690T_{Rb} - 0.3342 + \frac{5.79 \times 10^{-10}}{T_{Rb}^{32.75}}\right]P_c^{0.145} \qquad (15)$$

Values for parameter α calculated by using eq 14 and 15 are given in Table I for each of the 62 substances included in this study.

Correlation for Parameter β

Although the slope β is not as dominant as the corresponding intercept α, it is nonetheless a significant quantity for polar and quantum liquids. For this reason, the contribution of this parameter should be included for the more exacting prediction of saturated-liquid densities.

Nonpolar Substances. The factor s has been found useful in the correlation of parameter β, but in this case the inclusion of the quantum liquids to this category required the introduction of the additional parameter

$$\Lambda = P_c^{1/3}/(M^{1/2}T^{5/6}) \qquad (16)$$

This parameter is large for helium, hydrogen, and neon, but becomes relatively small for all other substances. The combined contribution of s and Λ defines β as follows:

$$\beta = 0.00318s - 0.0211 + 0.625\Lambda^{1.35} \qquad (17)$$

for nonpolar substances.

Polar Substances. The reduced dipole moment, Θ, has been employed to extend the application of eq 17 to include polar substances. This extension modifies eq 17 as follows:

$$\beta = 0.00318s - 0.0211 + 0.625\Lambda^{1.35} + 9.74 \times 10^6\Theta^{3.38} \qquad (18)$$

Equation 18 accommodates polar liquids, with the exception of water, alcohols, and carboxylic acids. For these hydroxyl-containing compounds, eq 18 must be modified.

Polar Compound Containing a Hydroxyl Group. The reduced dipole moment, Θ, has proven suitable for extending eq 17 to accommodate compounds that contain a hydroxyl group. For this class of compounds, eq 17 takes the form

$$\beta = 0.00318s - 0.0211 + 0.625\Lambda^{1.35} + 5.90\Theta^{0.835} \qquad (19)$$

Values for parameter β calculated by using eq 18 and 19 are presented in Table I for each of the 62 substances included in this study.

Table II. Basic Physical Constants, Density Parameters, and Sources of Data for Substances Used To Test the Method of This Study

										predicted			av	
	M	T_b, K	T_c, K	P_c, atm	μ, D	s	Λ	$10^3\Theta$	T_{Rb}	α	β	points	dev, %	ref
2,2,4-trimethylpentane	114.23	372.37	543.96	25.34	0	7.0146	0.0014	0	0.6846	0.2627	0.0013	23	2.55	*150, 158*
n-decane	142.29	447.3	617.7	20.76	0	7.9617	0.0011	0	0.7241	0.2458	0.0043	22	2.71	*138, 143, 144, 224*
n-dodecane	170.34	489.47	658.2	18.00	0	8.3847	0.0009	0	0.7496	0.2382	0.0056	21	4.63	*138, 143, 224*
dichloromethane	84.93	313.0	510.0	60.0	1.60	6.5052	0.0024	0.591	0.6137	0.2697	−0.0001	54	5.05	*167, 225–227*
chloroform	119.38	334.32	536.35	54.0	1.01	6.6010	0.0018	0.192	0.6233	0.2700	0.0000	54	3.45	*99, 135, 136, 167, 203*
bromobenzene	157.01	429.21	670.0	44.6	1.70	6.7695	0.0012	0.287	0.6406	0.2667	0.0005	51	2.15	*136, 137, 222*
aniline	93.13	457.6	699.0	52.4	1.53	7.5045	0.0017	0.251	0.6546	0.2537	0.0029	19	5.00	*99, 216*
naphthalene	128.17	491.14	748.4	39.98	0	7.0416	0.0012	0	0.6563	0.2623	0.0014	11	1.29	*166*
tin tetrachloride	260.50	387.3	591.9	37.0	0	6.8353	0.0010	0	0.6543	0.2659	0.0007	41	0.21	*137, 202*
												296	3.05 (av)	

Table III. Comparison of Actual and Calculated Critical Volumes for Nonpolar Substances

	v_c, cm^3/(g-mol)		
substance	actual	calcd	dev, %
monoatomic			
helium	57.52	61.24	6.47
neon	41.74	41.34	0.96
argon	75.50	75.39	0.15
krypton	91.18	92.83	1.81
xenon	119.5	120.6	0.92
diatomic			
n-hydrogen	64.98	67.15	3.34
p-hydrogen	64.13	66.96	4.41
nitrogen	89.50	89.20	0.34
oxygen	73.37	74.00	0.86
fluorine	66.22	66.06	0.24
chlorine	123.7	127.8	3.31
triatomic			
carbon dioxide	94.04	92.16	2.00
carbon disulfide	173.0	163.5	5.49
aliphatic hydrocarbons			
methane	98.42	100.6	2.21
ethylene	131.0	132.0	0.76
ethane	146.0	146.9	0.62
propylene	182.2	182.7	0.27
propane	201.8	200.6	0.59
2-methylpropane	263.0	254.9	3.08
n-butane	254.9	253.9	0.39
2-methylbutane	305.7	305.3	0.13
n-pentane	311.0	310.1	0.29
n-hexane	369.9	369.0	0.24
n-heptane	426.4	424.9	0.35
2,2,4-trimethylpentane	468.2	462.8	1.15
n-octane	492.4	483.0	1.91
naphthenes			
cyclopropane	162.8	165.7	1.78
cyclohexane	308.3	306.2	0.68
methylcyclohexane	367.8	368.4	0.16
aromatics			
benzene	258.7	258.5	0.08
toluene	315.6	319.0	1.08
o-xylene	368.6	367.6	0.27
m-xylene	376.5	377.7	0.32
p-xylene	379.2	378.0	0.32
naphthalene	413.5	402.8	2.59
miscellaneous			
carbon tetrachloride	275.9	276.9	0.36
tin tetrachloride	351.1	349.1	0.57
			1.36 (av)

Table IV. Comparison of Actual and Calculated Critical Volumes for Polar Substances

	v_c, cm^3/(g-mol)		
substance	actual	calcd	dev, %
diatomics			
carbon monoxide	93.06	90.81	2.42
hydrogen chloride	81.02	88.95	9.79
triatomics			
hydrogen sulfide	98.50	96.81	1.72
nitrous oxide	97.27	97.67	0.41
sulfur dioxide	122.0	116.3	4.67
miscellaneous			
ammonia	72.04	73.48	2.00
methyl chloride	139.1	135.4	2.66
chloroform	238.8	220.1	7.83
ethyl acetate	286.1	290.2	1.43
diethyl ether	279.7	281.9	0.79
diethylamine	301.0	291.4	3.19
pyridine	253.5	242.0	4.54
aniline	273.9	277.7	1.39
acetonitrile	173.2	183.9	6.18
propionitrile	229.5	241.7	5.32
acetone	208.9	217.2	3.97
chlorobenzene	308.4	310.5	0.68
bromobenzene	323.7	328.8	1.58
dimethyl sulfide	201.1	205.2	2.04
			3.30 (av)

Table V. Comparison of Actual and Calculated Critical Volumes for Substances with a Hydroxyl Group

	v_c, cm^3/(g-mol)		
substances	actual	calcd	dev, %
alcohols			
methanol	117.8	120.1	1.95
ethanol	167.2	166.5	0.42
2-propanol	220.4	230.0	4.36
1-propanol	218.2	216.7	0.69
2-methyl-1-propanol	272.5	266.3	2.28
2-butanol	268.6	266.3	0.86
2-methyl-2-propanol	274.5	271.8	0.98
1-butanol	274.5	265.2	3.39
1-pentanol	326.5	314.8	3.58
1-octanol	489.6	496.2	1.35
others			
water	57.19	54.76	4.25
acetic acid	171.1	186.1	8.77
			2.74 (av)

Application of Development and Its Extension to Other Substances

Equations 14 and 15 in conjunction with eq 18 and 19 permit the establishment of parameters α and β needed to define saturated-liquid densities for nonpolar and polar liquids through the relationship

$$\rho = \frac{MP_c}{RT_c} \frac{1}{[\alpha + \beta(1 - T_R)]^{1+(1-T_R)^{2/7}}} \tag{20}$$

The use of predicted values of α and β in eq 20 produces

Table VI. Comparative Evaluation of Methods for the Prediction of Saturated-Liquid Densities

substance	points	Riedel	Yen–Woods	Rackett	Spencer–Danner[b]	Joffe–Zudkevitch[c]	present method
monoatomics							
helium	164	7.84	14.93	16.34		4.43	1.02
neon	58	1.17	1.08	0.65	3.93	0.98	2.21
argon	128	0.84	0.79	0.80	0.32	0.55	0.22
krypton	81	0.49	1.04	1.47	0.49	0.52	1.04
xenon	67	2.32	1.95	1.78	2.67	1.31	2.65
diatomics							
n-hydrogen	54	5.26	7.80	8.03	0.96	1.72	1.28
p-hydrogen	49	4.67	8.14	8.71		2.35	0.96
nitrogen	111	0.40	0.54	0.42	0.41	0.41	1.06
oxygen	158	0.64	0.71	1.26	0.51	0.47	0.41
carbon monoxide	45	1.08	2.85	2.74	0.61	0.34	1.70
fluorine	103	0.84	0.58	0.37	0.37	0.44	1.15
chlorine	106	0.72	0.69	1.26	0.33	0.21	3.71
hydrogen chloride	53	2.92	9.74	10.93	0.38	0.53	4.81
polyatomics							
carbon dioxide	89	1.02	1.07	0.85	0.96	0.98	2.80
carbon disulfide	26	2.62	9.24	8.00	0.24	0.05	2.77
hydrogen sulfide	38	1.34	2.10	1.77	2.17	0.59	1.63
nitrous oxide	27	0.74	0.34	1.23	0.62	0.53	0.77
sulfur dioxide	56	1.10	2.12	1.68	1.02	0.33	6.34
ammonia	127	3.09	1.36	3.74	0.42	0.33	0.60
water	148	5.09	3.08	3.24		1.20	0.99
aliphatic hydrocarbons							
methane	104	0.96	1.61	2.12	0.32	0.59	1.07
ethylene	64	0.33	0.77	0.43	0.65	1.59	0.87
ethane	89	0.44	0.93	0.36	0.47	0.50	0.58
propylene	55	0.54	0.22	0.86	0.54	0.43	0.54
propane	152	0.78	2.48	1.60	0.46	0.86	0.42
2-methylpropane	116	1.92	5.46	4.73	0.41	0.17	0.87
n-butane	84	0.47	1.34	0.54	0.38	0.31	0.38
2-methylbutane	95	1.90	0.48	1.20	0.32	0.67	1.41
n-pentane	99	0.76	0.79	0.27	0.21	0.24	0.50
n-hexane	86	0.54	0.86	0.28	0.35	0.24	0.24
n-heptane	126	1.47	0.41	0.87	0.33	0.26	0.96
2,2,4-trimethylpentane	23	1.98	0.36	0.79	0.50	0.50	2.55
n-octane	69	0.49	2.12	1.17	0.43	0.19	1.43
n-decane[a]	22	2.57	0.70	1.52	0.56	0.45	2.71
n-dodecane[a]	21	3.20	1.40	1.71	0.10	0.52	4.63
naphthenes							
cyclopropane	25	1.10	0.44	0.54	0.53	0.48	2.08
cyclohexane	95	0.79	0.82	0.16	0.15	0.19	1.21
methylcyclohexane	59	1.25	0.33	1.02	0.36	0.36	0.70
aromatics							
benzene	202	0.63	1.60	0.87	0.21	0.27	0.79
toluene	125	0.36	0.43	0.81	0.24	0.25	1.32
o-xylene	103	0.61	0.78	0.30	0.51	0.35	0.29
m-xylene	105	0.30	1.18	0.38	0.43	0.15	1.19
p-xylene	83	0.49	1.40	0.45	0.32	0.16	1.46
naphthalene	11	3.28	6.26	5.40	0.11	0.17	1.29
alcohols							
methanol	102	3.82	1.35	9.31	3.59	0.47	0.93
ethanol	78	7.06	1.68	2.93	2.39	0.20	1.44
2-propanol	45	7.14	1.16	2.52	2.25	0.85	8.61
1-propanol	74	5.19	1.44	1.78	1.77	0.65	1.91
2-methyl-1-propanol	48	5.48	1.31	1.49		0.72	0.60
2-butanol	53	5.65	0.87	1.84		0.89	0.42
2-methyl-2-propanol	19	4.51	2.66	2.32		0.50	2.95
1-butanol	95	4.88	2.46	1.92	2.25	0.67	0.77
1-pentanol	63	5.73	1.69	1.07	0.78	0.82	1.98
1-octanol	63	6.62	0.54	0.78		0.32	4.44
miscellaneous							
methyl chloride	50	2.19	1.07	0.88	0.87	0.79	4.40
dichloromethane[a]	54	7.81	10.11	9.38	0.14	0.14	5.05
chloroform	54	4.35	11.24	10.72	0.25	0.09	3.45
carbon tetrachloride	137	0.33	0.55	0.26	0.16	0.21	0.29
ethyl acetate	64	0.27	0.42	1.44	0.30	0.22	1.64
diethyl ether	77	1.27	0.82	1.59	0.36	0.29	0.25
diethylamine	18	2.68	5.93	5.19	3.75	0.36	0.31
pyridine	28	4.56	8.51	7.58		0.08	0.42
aniline	19	7.18	6.18	8.94	0.34	0.05	5.00
acetonitrile	47	7.86	6.94	13.40	2.32	1.15	0.91
propionitrile	32	6.79	5.01	8.36	1.47	0.45	2.66
acetone	78	0.70	3.79	8.86	0.52	0.45	0.99
acetic acid	51	3.93	2.45	21.88	2.85	0.25	1.29
chlorobenzene	73	0.25	0.90	0.29	0.26	0.20	1.25

Table VI (Continued)

substance	points	Riedel	Yen–Woods	Rackett	Spencer–Danner[b]	Joffe–Zudkevitch[c]	present method
bromobenzene	51	0.24	0.30	0.79	0.16	0.13	2.15
dimethyl sulfide	23	0.97	0.91	1.17		0.46	2.49
tin tetrachloride	41	0.25	1.55	0.87		0.45	0.21
	5238	2.21 (av)	2.37 (av)	2.89 (av)	0.74 (av)	0.62 (av)	1.42 (av)

[a] Estimated values of ρ_c. [b] Blanks indicate that values of Z_{RA} for the Spencer–Danner method were not available. The resulting overall average deviation of 0.74% is based on a total of 4602 points. If z_c is used in place of Z_{RA}, the deviations become identical with those reported under the method of Rackett. [c] Since the quantum liquids helium, hydrogen, and neon are nonpolar, only one known density value for ech substance was used in the calculation of saturated-liquid densities by the method of Joffe and Zudkevitch. If two experimental liquid density values are used for each of these substances, their deviations decrease to 0.50% for helium, 0.30% for neon, 0.27% for n-hydrogen, and 0.44% for p-hydrogen.

calculated saturated-liquid densities that yield an overall average density deviation of 1.32% (4942 points) for the 62 substances. The deviation associated with each substance is given in Table I. These deviations show no discrimination between classes of compounds; however, somewhat excessive deviations were encountered with 2-propanol, sulfur dioxide, hydrogen chloride, 1-octanol, methyl chloride, and chlorine.

Saturated-liquid densities were calculated for nine polar and nonpolar substances not included in the development of this study. These substances are presented in Table II along with their basic physical constants and corresponding average density deviations. The overall average deviation for these compounds was found to be 3.05% (296 points) with a maximum of 5.05% (54 points) encountered with dichloromethane and a minimum of 0.21% (41 points) for tin tetrachloride.

Remarks Concerning Critical Volumes

When eq 20 is applied at $T_R = 1.00$, the corresponding critical density becomes

$$\rho_c = MP_c/(\alpha RT_c) \qquad (21)$$

If $\alpha = z_c$, then eq 21 defines rigorously the critical density. Equation 21 applies adequately to normally behaving liquids since α is in close proximity to z_c for substances of this type. However, for associating liquids and quantum liquids, parameter α is not in close proximity to z_c and therefore eq 20 will not yield reliable critical densities. This disparity becomes apparent upon reference to Figure 2 for water and Figure 3 for helium. For such substances, eq 20 has been found to apply well between the triple point and $T_R \approx 0.98$. However, for the calculation of average deviations associated with such substances, this temperature restriction was not considered and therefore eq 20 was applied up to $T_R = 1.00$.

The combination of eq 21 with eq 12 yields the critical volume for nonpolar substances

$$v_c = (RT_c/P_c)(0.3883 - 0.0179s) \qquad (22)$$

Table III presents a comparison of actual critical volumes and critical volumes calculated with eq 22 for the nonpolar substances included in this study. This comparison shows that the overall average deviation for critical volumes is 1.36% (37 substances). If the deviations for the quantum liquids helium and the two hydrogens are excluded, this dviation decreases to 1.07% (34 substances). Equation 22 has also been applied to a total of 46 additional hydrocarbons not included in Table III. These additional compounds include saturated aliphatic isomers through the octanes, acetylenes, olefins, 1,3-butadiene, naphthenes, and aromatics. For space economy, no table is presented for these hydrocarbons; however, the average deviation for their critical volumes was found to be 1.59% (46 substances) with a maximum of 4.43% encountered with 2,2,3,3-tetramethylbutane and a minimum of 0.03% for ethylbenzene.

For polar substances, not containing a hydroxyl group, the substitution of eq 14 into eq 21 yields the relationship

$$v_c = (RT_c/P_c)(0.3883 - 0.0179s - 130540\Theta^{2.41}) \qquad (23)$$

Table IV presents a comparison between actual critical volumes and critical volumes calculated with eq 23. The average deviation for these polar compounds is 3.30% (19 substances). Somewhat excessive deviations were encountered with hydrogen chloride, chloroform, acetonitrile, and propionitrile whose values exceed 5%.

For substances whose molecular structure contains a hydroxyl group such as water, acetic acid, and the alcohols, eq 15 can be substituted into eq 21 to define their critical volume as follows:

$$v_c = \frac{RT_c}{P_c^{0.855}}\left[0.690T_{Rb} - 0.3342 + \frac{5.79 \times 10^{-10}}{T_{Rb}^{32.75}}\right] \qquad (24)$$

Actual and calculated critical volumes are compared in Table V for the alcohols, water, and acetic acid with a resulting average deviation of 2.74% (12 substances). In this comparison, somewhat high deviations were encountered with 2-propanol, water, and acetic acid.

For the 68 substances of this study for which actual critical volumes were available, the combined average deviation of Tables III–V is 2.14%.

Comparison with Other Methods

The ability of other methods to predict saturated-liquid densities has been examined by using the 62 substances applied in the development of this study and the 9 additional compounds presented in Table II. Table VI presents the results of this comparative analysis for all 71 substances based on the present method and those of Riedel (*2*), Yen and Woods (*5*), Rackett (*6*), Spencer and Danner (*7*), and Joffe and Zudkevitch (*4*). This comparison indicates that the present method is capable of predicting saturated-liquid densities for all temperatures between the triple point and the critical point, with an overall average deviation of 1.42% (5238 points). The methods of Spencer–Danner (*7*) and Joffe–Zudkevitch (*4*) give rise to the lower average deviations of 0.74% (4602 points) and 0.62% (5238 points), respectively; however, each of these methods requires some knowledge of actual density behavior.

The earliest method of Riedel (*2*) presented in 1954 produced an average deviation of 2.21% (5238 points) and, were it not for the higher deviations encountered with the alcohols and other associated liquids, this deviation would be significantly lower. This fact is borne out by Joffe and Zudkevitch (*4*), who point to this issue as follows: "Although he did not explicitly mention that associated liquids do not conform to Riedel's liquid density correlation, it is reasonable to assume from his work that he was aware of this fact."

The Yen–Woods method (*5*) produced an average deviation of 2.37% (5238 points). Although their method does not discriminate against alcohols, this comparison indicates that excessive deviations are encountered with their method for dichloromethane (ρ_c = 0.440 g/cm^3, estimated), chloroform, pyridine, the nitriles, hydrogen chloride, helium, and hydrogen.

The Rackett method (*6*) described by eq 7 accommodates a variety of polar and nonpolar substances. For the 71 liquids, the average deviation was 2.89% (5238 points) and, with the exception of methanol, this method is capable of predicting reliable values for the alcohols. However, with the method of Rackett, excessive deviations were encountered with organic nitrogen-containing compounds, acetic acid, dichloromethane, chloroform, hydrogen chloride, and the quantum liquids helium and hydrogen.

Glossary

A, B, D	polynomials in z_c, eq 6
M	molecular weight
P	pressure, atm
P_c	critical pressure, atm
P_R	reduced pressure, P/P_c
R	gas constant
s	characterization factor, $T_{Rb} \ln P_c/(1 - T_{Rb})$
T	absolute temperature, K
T_b	normal boiling point, K
T_c	critical temperature, K
T_R	reduced temperature, T/T_c
T_{Rb}	reduced normal boiling point, T_b/T_c
v	molar volume, cm^3/(g-mol)
v_c	critical volume, cm^3(g-mol)
z	compressibility factor, Pv/RT
z_c	critical compressibility factor, $P_c v_c/(RT_c)$
Z_{RA}	adjustable constant, eq 8

Greek Letters

α, β	parameters, eq 10
α_c	Riedel factor, $(d \ln P_R/d \ln T_R)_{T_R=1.00}$, eq 3
Θ	reduced dipole moment, $\mu^2 P_c/T_c^2$, eq 13
Λ	quantum parameter, $P_c^{1/3}/(M^{1/2} T_c^{5/6})$, eq 16
μ	dipole moment, D
ρ	density, g/cm^3
ρ_c	critical density, g/cm^3
ρ_R	reduced density, ρ/ρ_c

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