J. Chem. Eng. Data **1986**, *31*, 265-266

Volume Ratio Measurements for Tetrachloromethane under Pressure at 308, 318, and 338 K

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Volume ratios for tetrachloromethane at 308, 318, and 338 K and pressures up to 150, 181, and 250 MPa, respectively, have been determined by using a bellows volumometer, with overall accuracy within ±0.04%. The results extend the pressure range of previous data (maximum pressure 100 MPa) in the literature.

1. Introduction

Measurements of the $p-V-T$ behavior of tetrachloromethane were made by Gibson and Loeffler (*1*) at 25-MPa intervals up to a maximum pressure of 100 MPa for five temperatures in the range 298.15–338.15 K. The only data at pressures above 100 MPa were the relative volumes of Bridgman (*2*) tabulated at 50-MPa intervals up to 150 and 350 MPa for 323 and 368 K, respectively. For both sets of data there was uncertainty about the values below 50 MPa in ref *2* and 25 MPa in ref *1*.

The present measurements are at three of the temperatures used by Gibson and Loeffler (*1*) but extend to pressures closer to the freezing pressures and involve several measurements below 25 MPa at each temperature.

2. Experimental Section

The volume ratio measurements were made with a bellows volumometer which has been described elsewhere (*3*, *4*). The basic equation for the measurements is

$$k = V_p/V_{p^0} = 1 - (A/V_{p^0})(l_{p^0} - l_p) \qquad (1)$$

with A the effective cross-sectional area of the bellows, V_p and V_{p^0} the volume of the volumometer cell at pressures p and 0.1 MPa and $\Delta l = l_{p^0} - l_p$ the change in length of the bellows resulting from application of pressure p.

Because A/V_p^0 depends on Δl the volumometer is usually calibrated with water and n-heptane and the dependence of A/V_{p^0} at each temperature represented by a cubic equation in Δl. Before the present work the instrument had been calibrated at 278, 288, 298, 313, and 323 K. Therefore for the measurements at 308 and 318 K the necessary A/V_{p^0} values were obtained by linear interpolation of those at 298 and 313 K and 313 and 323 K, respectively. For the measurements at 338 K the volumometer was calibrated with methanol and n-heptane. For methanol the volume ratios, k, were calculated from the equation given by Machado and Street (*5*). For n-heptane the volume ratios were obtained by extrapolation to 338 K of the data given at 273, 298, 313, and 333 K by Eduljee, Newitt, and Weale (*6*).

The overall accuracy in A/V_{p^0} is estimated as ±0.1%. Values of Δl obtained from the experimental measurements are generally accurate to ±0.05% so that the overall error in $[1 - V_p/V_{p^0}]$ is ±0.15% corresponding to a maximum error in the V_p/V_{p^0} of Table I of ±0.04%.

Table I. Volume Ratios for Tetrachloromethane[a]

p/MPa	V_p/V_{p^0}
T = 308.15 K	
1.05	0.9989 (0.9989)
3.64	0.9963 (0.9960)
8.60	0.9914 (0.9907)
13.73	0.9863 (0.9855)
18.43	0.9818 (0.9810)
23.64	0.9770 (0.9762)
29.8	0.9716 (0.9709)
39.7	0.9635 (0.9629)
49.9	0.9559 (0.9553)
60.2	0.9490 (0.9483)
69.9	0.9428 (0.9421)
79.8	0.9370 (0.9362)
89.8	0.9313 (0.9306)
100.0	0.9258 (0.9252)
110.8	0.9202
119.8	0.9159
130.1	0.9113
140.3	0.9070
150.3	0.9026
T = 318.15 K	
1.40	0.9983 (0.9984)
4.34	0.9949 (0.9948)
9.22	0.9894 (0.9892)
14.45	0.9839 (0.9836)
18.67	0.9796 (0.9793)
24.83	0.9737 (0.9733)
30.1	0.9690 (0.9685)
39.6	0.9609 (0.9604)
49.8	0.9529 (0.9524)
60.5	0.9452 (0.9448)
69.8	0.9390 (0.9386)
80.0	0.9326 (0.9322)
90.2	0.9267 (0.9263)
100.0	0.9212 (0.9209)
110.0	0.9160
120.0	0.9110
130.0	0.9063
140.7	0.9015
150.2	0.8974
160.1	0.8933
167.7	0.8903
181.5	0.8852
T = 338.15 K	
2.76	0.9961 (0.9961)
5.11	0.9930 (0.9928)
10.21	0.9864 (0.9861)
15.22	0.9803 (0.9799)
20.23	0.9746 (0.9741)
30.1	0.9642 (0.9637)
39.1	0.9556 (0.9551)
49.6	0.9466 (0.9460)
59.7	0.9387 (0.9380)
69.7	0.9314 (0.9307)
79.9	0.9246 (0.9238)
90.0	0.9183 (0.9174)
100.3	0.9122 (0.9114)
110.0	0.9069
120.1	0.9016
129.3	0.8970
139.9	0.8920
150.4	0.8873
170.8	0.8788
190.3	0.8713
210.2	0.8642
230.5	0.8575
250.2	0.8515

[a] Values in parentheses calculated from eq 2 by using coefficients given in ref *1*.

Temperatures were held constant to ±0.005 K and were measured to ±0.01 K. Pressures were measured with two Heise-Bourdon gauges recently calibrated with a dead-weight gauge; up to 25 MPa the readings should be accurate to ±0.025 MPa and to ±0.2 MPa above that pressure. The carbon tetrachloride was of analytical reagent grade, conforming to ACS standard, that had been dried with a type 4A molecular sieve for several months; low levels of impurities have an insignificant effect on the volume ratio.

3. Results and Discussion

The volume ratios obtained from the measurements are given in Table I. Gibson and Loeffler (*1*) expressed their results at each temperature by means of the coefficients of eq 2. Those

$$1 - k = C \log [(B + p)/(B + p^0)] \qquad (2)$$

coefficients (converted to SI units) have been used to generate the volume ratios, k, included for purposes of comparison in

0021-9568/86/1731-0265$01.50/0

Table II. Coefficients of Eq 3 for Tetrachloromethane[a]

T/K	a_0/MPa	a_1	$-a_2$/GPa^{-1}	a_3/GPa^{-2}	δK/%
308.15	981.42525	1.490071	−36.3279	−144.2981	0.55
318.15	830.97643	4.74349	3.81929	2.24447	0.06
338.15	700.55304	4.84812	4.99263	5.31830	0.07

[a] The average deviation in K in column 6 (see eq 3) corresponds to roughly $^1/_{10}$ that deviation in the volume ratio.

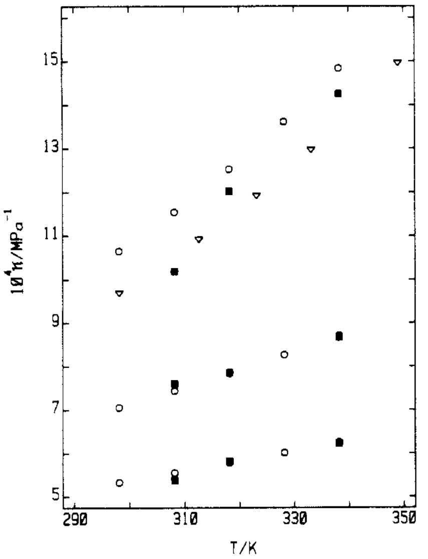

Figure 1. Isothermal compressibility of carbon tetrachloride: uppermost values, 0.1 MPa; middle, 50 MPa; bottom, 100 MPa; circles, ref *1*; squares, this work; triangles, ref *7*.

Table I. The agreement between the two sets of values is generally excellent although the volume ratios presented here are consistently slightly higher than those calculated from ref *1*. It is of some interest to note that if eq 2 is used (with the coefficients from ref *1*) to calculate volume ratios above 100 MPa (the highest pressure used in ref *1*), there is still excellent agreement with the present data up to 150 MPa at all three temperatures.

Although equations of the form of eq 2 provide a reliable method of extrapolating outside the pressure range of the measurements they represent, such equations do not fit the measured volume ratios as well as secant bulk modulus equations, usually of third order, of the form

$$K = p/(1 - k) = \sum_{i=0}^{n} a(i)p^i \qquad (3)$$

Coefficients of eq 3 which provide a good fit to the present results are given in Table II.

Isothermal compressibilities, κ, can be obtained from the volume ratios since

$$\kappa = -(1/V)(\partial p)_T = -(1/k)(\partial k/\partial p)_T$$
$$= -(1/(p - K))(1 - (p/K)(\partial K/\partial p)_T) \qquad (4)$$

Values of κ obtained from eq 3 and 4 are shown in Figure 1 where they are compared with those obtained from Gibson and Loeffler (*1*) (eq 1 and 4) and Holder and Whalley (*7*). Overall there is the expected close agreement between κ from the present measurements and those from Gibson and Loeffler; the greatest difference is found at 308.15 K. The systematic difference from Holder and Whalley is difficult to explain although it should be remembered that the present data and those of ref *1* are less accurate the lower the pressure and that both Gibson and Loeffler and Holder and Whalley used mercury to transmit the pressure.

Registry No. Tetrachloromethane, 56-23-5.

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Received for review June 14, 1985. Accepted December 16, 1985.

Vapor Pressures of Poly(dimethylsiloxane) Oligomers

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Vapor pressures of seven linear, seven cyclic, and two branched dimethylsiloxane oligomers have been measured over the pressure range 7–133 kPa (50–1000 Torr). The experimental data were fitted by the Antoine equation. Extrapolations of these data to the critical point were made by using literature or estimated critical constants and the Halm–Stiel extension of Pitzer's vapor pressure equation. Constants for the Halm–Stiel equation are given. The extrapolated data were also fit to the AIChE DIPPR vapor pressure equation.

Introduction

For engineering calculations we required vapor pressure of low molecular weight cyclic, linear, and branched poly(dimethylsiloxanes). Data were necessary which extend to the critical point. Critical points are known for many of these oligomers, but vapor pressure data near the critical have been measured for only two. Also, examination of the literature showed remarkable variations in the reported vapor pressure for all of them (*1–18*). For these reasons we have remeasured vapor pressure for the linear compounds from hexamethyldisiloxane through hexadecamethyloctasiloxane, cyclic compounds from hexamethylcyclotrisiloxane through octadecamethylcyclononasiloxane, and the two branched compounds methyltris(trimethylsiloxy)silane and tetrakis(trimethylsiloxy)silane. No literature vapor pressure data were found for the branched compounds.

Because all of these compounds have very long names, the system of abbreviation introduced by Wilcock (*1*) will be used. All of the compounds can be said to be made up of four structural groups, the monofunctional trimethylsiloxy group, $(CH_3)_3SiO_{1/2}$ (M), the difunctional dimethylsiloxy group, $(CH_3)_2SiO$

0021-9568/86/1731-0266$01.50/0