

## **Volume Ratios for *n*-Pentane in the Temperature Range 278–338 K and at Pressures up to 280 MPa**

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Volume ratios ( $V_p/V_{0.1}$ ), and isothermal compressibilities calculated from them, are reported for *n*-pentane for seven temperatures in the range 278 to 338 K for pressures up to 280 MPa. The isobaric measurements were made with a bellows volumometer for which a novel technique had to be devised to enable measurements to be made above the normal boiling point (309.3 K). The accuracy of the volume ratios is estimated to be  $\pm 0.05$  to 0.1% up to 303.15 K and  $\pm 0.1$  to 0.2% from 313.15 to 338.15 K. The volume ratios are in good agreement with those calculated from recent literature data up to the maximum pressure of the latter, viz., 60 MPa.

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**KEY WORDS:** high pressure; isothermal compressibility; *n*-pentane; volume ratio.

### **1. INTRODUCTION**

Isochoric ( $p, \rho, T$ ) measurements for *n*-pentane over the temperature range 238–473 K at pressures up to 60 MPa have been reported by Kratzke and co-workers [1]. Previous isochoric measurements by Gehrig and Lentz [2] covered the temperature range 313 to 643 K up to a maximum pressure of 243 MPa (at the highest temperatures) but only to 138 MPa up to 343 K; the isothermal pressure ranges were such that smoothed molar volumes were reported only up to 50 MPa over the entire temperature range. Moreover, the uncertainty in these [2] volume determinations was

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subsequently estimated [1] to be up to 1.7%, so that there is a lack of high-accuracy ( $p, V, T$ ) data for  $n$ -pentane at pressures above 60 MPa.

The objective of the present study was to extend the available ( $p, V, T$ ) data to about 280 MPa for temperatures from 278 to 338 K by using a bellows volumometer [3–5] to determine volume ratios as a function of temperature and pressure. In combination with densities at 0.1 MPa, the volume ratios provide the required ( $p, V, T$ ) data.

Because the normal boiling point of  $n$ -pentane is lower than three of the temperatures of the present measurements, the usual experimental procedure and treatment of the experimental data had to be modified to enable the measurements to be made at pressures close to 0.1 MPa. The normal procedure with the bellows volumometer is to begin with the bellows fully extended at 0.1 MPa at each temperature at which measurements are to be made. For the measurements above the normal boiling point the bellows was initially compressed (and the cell closed) at 0.1 MPa and 303.15 K (below the normal boiling point of 309.3 K), by an amount estimated to be sufficient to contain the liquid volume at the saturated vapor pressure of the highest temperature of the measurements. This procedure requires corrections to be applied to the calibration factors of the volumometer to enable calculation of the volume ratios. These corrections are explained in detail below, because they enable the temperature range for which the bellows volumometer technique is normally applicable to be extended to the liquified gas regime. The effect of the corrections is that the volume ratios above the normal boiling point are less accurate than those at the lower temperatures.

## 2. EXPERIMENTAL

The  $n$ -pentane was May and Baker “Pronalys AR” grade used as received except for treatment with molecular sieve to remove water. The stated purity of the material was  $\geq 99.0\%$ , and it is unlikely that the residual impurities would have had a significant effect on the measured volume ratios.

Temperatures were maintained constant to within  $\pm 0.005$  K and were measured with an accuracy of  $\pm 0.01$  K using a calibrated platinum resistance thermometer. Two Heise Bourdon tube gauges which had been calibrated against deadweight testers were used to measure pressures. Up to 25 MPa pressures were measured to  $\pm 0.01$  MPa with a 0- to 25-MPa gauge, and at higher pressures a 0- to 300-MPa gauge gave pressures to  $\pm 0.1$  MPa.

The basic equation for the bellows volumometer is

$$k = V_p/V_{0.1} = 1 - (A/V_{0.1})(l_{0.1} - l_p) \quad (1)$$

where  $V_{0.1}$  and  $V_p$  are the volumes of the volumometer cell at 0.1 MPa and pressure  $p$ , respectively,  $A$  is the effective cross-sectional area of the bellows, and  $\Delta l = l_{0.1} - l_p$  is the change in length of the bellows resulting from the pressure change  $p - 0.1$ .  $A/V_{0.1}$  depends on  $\Delta l$  and has been determined by calibration with liquids such as water whose volume ratios are known, at 278, 288, 298, 303, 313, 323, and 338 K. In effect, at any temperature at which the volumometer has been calibrated  $A/V_{0.1}$  is known as a function of  $\Delta l$ , and in normal operation neither  $A$  nor  $V_{0.1}$  needs to be evaluated separately.

The normal operating procedure is to close the volumometer at 0.1 MPa with the bellows fully extended, when thermal equilibrium has been attained at each temperature at which measurements are to be made. The pressure is then raised to about 280 MPa (or a maximum pressure slightly smaller than the freezing pressure, if the freezing pressure is below 280 MPa). After reattainment of thermal equilibrium, 23 (for a maximum pressure of 280 MPa) measurements of  $l_p$  are made at pressures decreasing from 280 to about 2.5 MPa, at pressure intervals which become smaller as the pressure is reduced. The values of  $l_p$  are curve fitted to a polynomial in  $p$ , and  $l_{0.1}$  is obtained as the intercept of the fitted curve. Values of  $\Delta l$  so obtained are generally accurate to  $\pm 0.05\%$ , corresponding to a maximum error in  $V_p/V_{0.1}$  of  $\pm 0.04\%$ , except that the uncertainty in  $V_p/V_{0.1}$  increases at pressures below 50 MPa to about  $\pm 0.1\%$  at pressures close to 0.1 MPa. This procedure was followed for *n*-pentane at temperatures up to 303 K. Following the measurements at 303 K, the volumometer was opened to the atmosphere and a spacer about 12 mm long used to partially compress the bellows. The length of the spacer was based on an estimate of the density of *n*-pentane at the saturated vapor pressure for the highest intended temperature of the measurements. The volumometer was then closed and, with the spacer removed, pressurized to above the saturated vapor pressure at 313 K, and the temperature raised to 313 K. The usual process of taking measurements at pressures decreasing from about 280 to about 2.5 MPa was then followed. Subsequently the volumometer was heated to 323 and 338 K, and measurements made at these temperatures in the same fashion except that a minimum pressure of 9.8 MPa was used at 338 K.

Application of Eq. (1) to *n*-pentane, for  $T > 303$  K, requires two correction factors, a volume correction  $\Phi_{V,T}$  and an area correction  $\Phi_{A,T}$ , to be evaluated. The corrected  $A/V_{0.1}$  values are given at any temperature by

$$(A/V_{0.1})_{T'} = (A/V_{0.1})_T \Phi_{V,T} \Phi_{A,T} \quad (2)$$

where the prime signifies that the bellows is not fully extended at 0.1 MPa.

The volume correction factor,  $\Phi_{V,T}$ , allows for the volume expansion of the *n*-pentane contained in the cell at 303.15 K as a result of temperature increase and the counteracting increase in volume of the cell material, stainless steel. It is evaluated from

$$\begin{aligned}\Phi_{V,T} &= V_{0.1,T}/V'_{0.1,T} \\ &= V_{0.1,T}/\{V'_{0.1,303\text{ K}}[1 + \alpha_1(T - 303.15) - \alpha_{ss}(T - 303.15)]\} \quad (3)\end{aligned}$$

In Eq. (3)  $V_{0.1,T}$  is the volume contained by the volumeter at temperature  $T$  with the bellows fully extended,  $V'_{0.1,303\text{ K}}$  is the volume contained at 303.15 K with the spacer in place,  $V'_{0.1,T}$  is the corresponding volume at temperature  $T$ , and  $\alpha_1$  and  $\alpha_{ss}$  are isobaric expansivities at 0.1 MPa of *n*-pentane and the stainless steel from which the volumeter was fabricated. The liquid expansivity was calculated from the densities for *n*-pentane (given by Timmermans [6]) fitted to the equation

$$\rho = 0.80205_5 - 2.16249 \times 10^{-4}T - 1.30806 \times 10^{-6}T^2 \quad (4)$$

( $273.15 \leq T \leq 303.15$  K), where  $\rho$  is in  $\text{g} \cdot \text{cm}^{-3}$  and  $T$  is in K. We have followed Bridgman [7] in extrapolating Eq. (4) to obtain densities and hence expansivities at 313.15, 323.15, and 338.15 K. The volume of the volumeter at 0.1 MPa with the bellows fully extended had been previously determined at several temperatures using water and is represented by

$$V_{0.1,T} = 52.62897 + 7.40507 \times 10^{-4}T + 3.06817 \times 10^{-5}T^2 \quad (5)$$

( $V_{0.1,T}$  in  $\text{cm}^3$ ,  $T$  in K). The quantity  $\alpha_{ss}$  was evaluated as a function of temperature from the coefficients of Eq. (5).

The area correction factor in Eq. (2) makes allowance for the effect of the spacer on the effective cross-sectional area of the bellows and is given by

$$\Phi_{A,T} = A'_{0.1,T}/A_{0.1,T} \quad (6)$$

where the prime has the same connotation as before. Since it is difficult to measure  $A'_{0.1,T}$ , the volume of the volumeter at 0.1 MPa and 303.15 K was determined using three spacers of lengths 1.211<sub>5</sub>, 2.465<sub>6</sub>, and 3.735<sub>6</sub> cm. Together with the volume corresponding to zero spacer length from Eq. (5), these volumes are represented with root mean square deviation in  $V$  of 0.05  $\text{cm}^3$  by

$$V_{0.1,303\text{ K}} = a_0 + a_1l_s + a_2l_s^2 \quad (7)$$

(with  $a_0 = 57.67285$ ,  $a_1 = -3.694408$ ,  $a_2 = 0.1054528$ ), where  $l_s$  is the spacer length in cm. The decrease in volume due to a spacer of length  $l_s$  is then

$$\Delta V_{0.1,303\text{ K}} = -(a_1 l_s + a_2 l_s^2) \quad (8)$$

The average cross-sectional area corresponding to a spacer of length  $l_s$  is

$$\begin{aligned} \bar{A}_{0.1,303\text{ K}} &= -\Delta V_{0.1,303\text{ K}}/l_s \\ &= -(a_1 + a_2 l_s) \end{aligned} \quad (9)$$

and when  $l_s = 0$

$$A_{0.1,303\text{ K}} = -a_1 \quad (10)$$

We now make the approximation that for a given bellows displacement,  $\Delta l_{0.1,T}$ ,

$$\begin{aligned} A'_{0.1,T}/A_{0.1,T} &= A'_{0.1,303\text{ K}}/A_{0.1,303\text{ K}} \\ &= \bar{A}_{0.1,303\text{ K}}/A_{0.1,303\text{ K}} \end{aligned} \quad (11)$$

where  $\bar{A}_{0.1,303\text{ K}}$  is the effective cross-sectional area at 303 K corresponding to a spacer of length  $l_s = \Delta l_{0.1,T}$ . Since  $\Delta l_{0.1,T}$  cannot be measured,  $\bar{A}_{0.1,303\text{ K}}$  cannot be evaluated directly from Eq. (9) with  $l_s = \Delta l_{0.1,T}$  and is determined as follows. Since

$$\Delta V_{0.1,T} = V_{0.1,T} - V'_{0.1,T} \quad (12)$$

[with  $V_{0.1,T}$  from Eq. (7) and  $V'_{0.1,T}$  from the denominator of Eq. (3)], and in addition,

$$\begin{aligned} \Delta V_{0.1,T} &= \Delta l_{0.1,T} A'_{0.1,T} \\ &= \Delta l_{0.1,T} \bar{A}_{0.1,303\text{ K}} \end{aligned} \quad (13)$$

[with  $\bar{A}_{0.1,303\text{ K}}$  from Eq. (9) with the substitution  $l_s = \Delta l_{0.1,T}$ ],  $\Delta l_{0.1,T}$  and hence  $\bar{A}_{0.1,303\text{ K}}$  and  $\Phi_{A,T}$  can be evaluated at each temperature  $T > 303.15\text{ K}$  from Eqs. (6), (10), (11), (12), and (13). The values of  $\Phi_{V,T}$  and  $\Phi_{A,T}$  are as follows: 313.15 K— $\Phi_{V,T}$ , 1.0745 and  $\Phi_{A,T}$ , 0.9709; 323.15 K—1.0577 and 0.9773; and 338.15 K—1.0322 and 0.9871.

### 3. RESULTS AND DISCUSSION

Volume ratios were expressed as the secant bulk modulus,  $K$ , defined by

$$K = p/(1 - k) \quad (14)$$

**Table I.** Coefficients of Eq. (15) for Secant Bulk Modulus<sup>a</sup>

$T$ (K)	$B_0$ (MPa)	$B_1$	$-10^3 B_2$ (MPa <sup>-1</sup> )	$10^6 B_3$ (MPa <sup>-2</sup> )	$\sigma$ (%)
278.15	605.35400	4.75243	5.19297	5.79771	0.10
288.15	553.11797	4.66991	5.14958	5.87278	0.13
298.15	495.97542	4.57105	4.19476	2.54208	0.24
303.15	476.44447	4.55360	4.51445	3.22509	0.23
313.15	427.94452	4.61013	5.09036	4.26893	0.26
323.15	383.16966	4.47804	4.90572	3.76434	0.33
338.15	333.29836	4.25541	4.70007	3.37822	0.26

<sup>a</sup>  $K$  = secant bulk modulus.

and fitted to equations of the form

$$K = \sum_{i=0}^3 B_i p^i \quad (15)$$

The coefficients of Eq. (15) are given in Table I. For  $T \leq 303.15$  K, the overall uncertainty of the volume ratio determinations corresponds to about  $\pm 0.04\%$  in density at pressure above 50 MPa, increasing to about  $\pm 0.1\%$  at pressures approaching 0.1 MPa. The comparison in Table II of

**Table II.** Comparison of Volume Ratios ( $V_p/V_{0.1}$ )

$T$ (K)	$p$ (MPa)					Source <sup>a</sup>
	0.1	10	20	40	60	
278.15	0.9998	0.9847	0.9714	0.9492	0.9313	A
	0.9999	0.9843	0.9710	0.9492	0.9315	B
288.15	0.9998	0.9833	0.9690	0.9454	0.9265	A
	1.0000	0.9829	0.9685	0.9452	0.9266	B
298.15	0.9998	0.9815	0.9659	0.9405	0.9206	A
	1.0000	0.9812	0.9656	0.9408	0.9212	B
303.15	0.9998	0.9808	0.9646	0.9386	0.9183	A
	1.0000	0.9803	0.9640	0.9383	0.9183	B
313.15	0.9998	0.9789	0.9614	0.9338	0.9127	A
	1.0000	0.9782	0.9605	0.9331	0.9120	B
323.15	0.9997	0.9766	0.9575	0.9279	0.9055	A
	1.0000	0.9758	0.9566	0.9273	0.9052	B
338.15	0.9997	0.9734	0.9520	0.9194	0.8952	A
	1.0000	0.9718	0.9498	0.9176	0.8938	B

<sup>a</sup> A, this work; B, Ref. 1.

the present volume ratios with those calculated from the equation of state [Eq. (13) in Ref. 1] given by Kratzke and co-workers gives an indication of the accuracy of the procedure we have used. (An error of  $\leq 0.05\%$  in density is claimed in Ref. 1.) For  $T \leq 303.15$  K the agreement is within the expected uncertainty of the usual volumometer procedures. For  $T > 303.15$  K the comparison indicates that the uncertainty in density from the present measurement is probably between 0.1 and 0.2%. The equation of state [1] also gives an independent estimate of the density of *n*-pentane at 0.1 MPa and  $T \geq 313$  K to compare with that obtained by extrapolation of Eq. (4). The agreement is always better than 1 in 50,000.

An extensive comparison with the measurements of Gehrig and Lentz [2] is possible only at 323.15 K and up to 120 MPa by using their coefficients (Table 2 in Ref. 2) for the modified Tait equation to obtain the ratio  $V_p/V_{16.52}$ . There appears to be a systematic error increasing with pressure in the data of Ref. 2 at 323.15 K: the agreement with the present data is  $\leq 0.1\%$  up to 60 MPa but thereafter the difference steadily increases to 0.7% at 120 MPa. This finding supports the comment in Ref. 1 that the volumes of Ref. 2 were "accurate to within 0.3 to 1.7%."

Bridgman [7] gave specific volumes at 273.15, 323.15, and 368.15 K. At 323.15 K, where a direct comparison with the present results is possible, there is poor agreement with his results. For example, at 100 MPa Ref. 7 provides 0.865 for  $V_p/V_{0.1}$ , while the present results give 0.8727.

Isothermal compressibilities,  $\kappa$ , were calculated from the coefficients of Eq. (15) using the relationships

$$\begin{aligned}\kappa &= (1/V)(\partial V/\partial p)_T \\ &= -[1/(p-K)][1 - (p/K)(\partial K/\partial p)_T]\end{aligned}\quad (16)$$

Table III. Isothermal Compressibility of *n*-Pentane<sup>a</sup>

<i>p</i> (MPa)	<i>T</i> (K)						
	278.15	288.15	298.15	303.15	313.15	323.15	338.15
0.1	16.5	18.0	20.1	21.0			
20	12.8	13.8	15.0	15.5	16.7	18.1	20.3
50	9.51	10.1	10.7	10.9	11.4	12.2	13.3
100	6.68	6.96	7.17	7.33	7.52	7.88	8.49
150	5.22	5.40	5.53	5.67	5.80	6.06	6.52
200	4.32	4.44	4.64	4.76	4.87	5.11	5.54
250	3.67	3.74	4.11	4.20	4.27	4.54	4.98
275	3.38	3.43	3.92	3.99	4.04	4.32	4.77

<sup>a</sup> Units of isothermal compressibility:  $10^4$  MPa<sup>-1</sup>.

The values of  $\kappa$  are given in Table III. For temperatures up to 303.15 K, the probable uncertainty in  $\kappa$  is  $\pm 1\%$  for  $p \geq 50$  MPa, increasing to  $\pm 2\%$  at 0.1 MPa. At the higher temperatures the uncertainty in  $\kappa$  should be within  $\pm 2\%$  for  $p \geq 50$  MPa, increasing to about  $\pm 4\%$  at pressures approaching 0.1 MPa. The variation of  $\kappa$  with pressure and temperature is similar to that of other saturated hydrocarbons, namely, an increase with increasing temperature at constant pressure and a decrease with increasing pressure at constant temperature.

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