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Density and Virial Coefficients of Gaseous Butane from 265 to 450 K at Pressures to 3.3 MPa

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The Burnett-isochoric (B-I) method has been used to measure gas densities and virial coefficients for butane from 265 to 450 K (IPTS, 1990; Preston-Thomas, 1990). Two independent B-I runs were performed but both with a base isotherm of 450 K, which is well above the critical temperature of 425 K. Significant physical adsorption of butane molecules onto the highly-polished, stainless steel cell walls was found below 375 K in agreement with conclusions reached by Ewing and associates in comparing their sonic-velocity-based density virial coefficients with those from the $P-V-T$ literature. Our data below 375 K were then corrected for adsorption errors by previously published procedures developed by our laboratory for highly polar gases. Using statistical weighting of our two B-I runs, recommended density second virial coefficients $B(T)$ are reported from 265 to 450 K whereas third virial coefficients $C(T)$ are reported only from 325 to 450 K as values below 325 K are too uncertain due to the vapor pressure dropping under 300 kPa. However, then the virial equation of state truncated after $B(T)$ is sufficient to represent the gas densities. At the lower temperatures of this investigation, our $B(T)$ values lie between those from sonic velocities and the more negative values from the $P-V-T$ literature, which are uncorrected for adsorption errors; we are closer to the values from sonic velocities and about $^1/_4$ of the way between the two sets. At the higher temperatures, we agree very closely with the better $P-V-T$ measurements whereas the sonic-velocity-based values become increasingly more negative.

Introduction

A considerable amount of literature of $P-V-T$ measurements exists for gaseous butane, an important *n*-alkane hydrocarbon, as summarized by Dymond and Smith (1980). However, Ewing et al. (1988) found that values of the density second virial coefficient $B(T)$ from 250 K to 320 K, as calculated from their sonic velocity measurements using a much improved spherical acoustic resonator, were divergently less negative at lower temperature (see Figure 1). Ewing et al. (1988) concluded that these differences were due to adsorption errors in the $P-V-T$ (density) measurements.

While sound speeds can now be measured to precisions of 5−10 ppm in gases, the weak link is the identity connecting the sonic second virial coefficient β_a with $B(T)$

$$(\beta_a/2) \equiv B + (\gamma^* - 1)T(\mathrm{d}B/\mathrm{d}T) + \{[(\gamma^* - 1)T]^2/2\gamma^*\}(\mathrm{d}^2B/\mathrm{d}T^2) \quad (1)$$

where γ^* is the ratio of the isobaric to isochoric perfect gas heat capacities, which also may be determined from the sonic first virial coefficient, $W_0{}^2 = (RT\gamma^*/M)$, where M is the molecular weight. The acoustic virial equation of state, in terms of a Taylor series with pressure as the independent variable, is

$$W^2 = W_0{}^2[1 + (\beta_a P/RT) + (\gamma_a P^2/RT) + ...] \quad (2)$$

where W is the sound speed and γ_a is the acoustic third virial coefficient. In order to use eq 1 to calculate $B(T)$, it is obvious that *the form* of the temperature dependency of B must be assumed. This is commonly taken from either a molecular model (e.g., Lennard-Jones) or an empirical equation of state (EoS). To check the propagation of various random and systematic experimental errors in γ^* and β_a into values calculated for $B(T)$, a density EoS can be used to calculate *perfect* values of $W(P,T)$. These can then be reduced using eq 1; if the data reduction assumes the same temperature dependency for $B(T)$ as that corresponding to the density EoS, then $B(T)$ calculated from eq 1 will agree with the known *true* values of the original density EoS used to generate the sound speeds. If a different temperature dependency is assumed, then small but significant errors result (Eubank et al., 1994). This reference superimposed various random and systematic errors onto the *perfect* values of $W(P,T)$, calculated from a Redlich−Kwong EoS for butane. Perhaps surprisingly, the random errors propagated systematically due to eq 1 being a differential equation. It was found that sonic data must be of high precision (±10 ppm) to generate $B(T)$ equal to ±1 cm^3/mol. Except perhaps for adsorption errors, which are much smaller than for corresponding $P-V-T$ experiments but not zero, systematic errors in the sonic velocity measurements appear unimportant to $B(T)$—likely because so many derivatives of W have been taken so fixed errors are mostly eliminated.

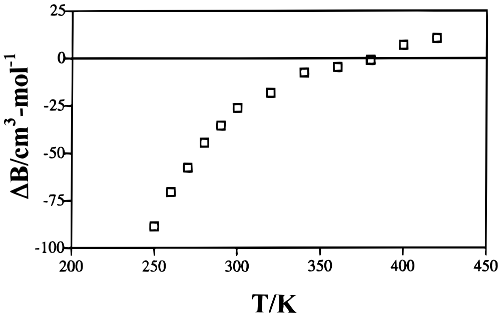

Figure 1. Deviations $\Delta B = B(T) - B(\text{sonic})$, where $B(T)$ is from Dymond and Smith (1980), based upon selected $P-V-T$ data, and B(sonic) is from Ewing et al. (1988).

This experimental study was undertaken for butane because of the disagreement (Figure 1) in the literature,

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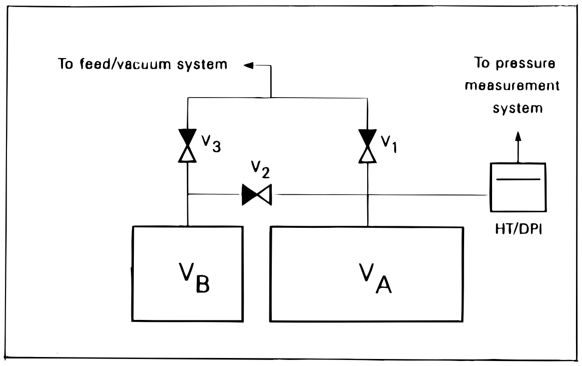

Figure 2. Schematic of the Burnett-isochoric cell.

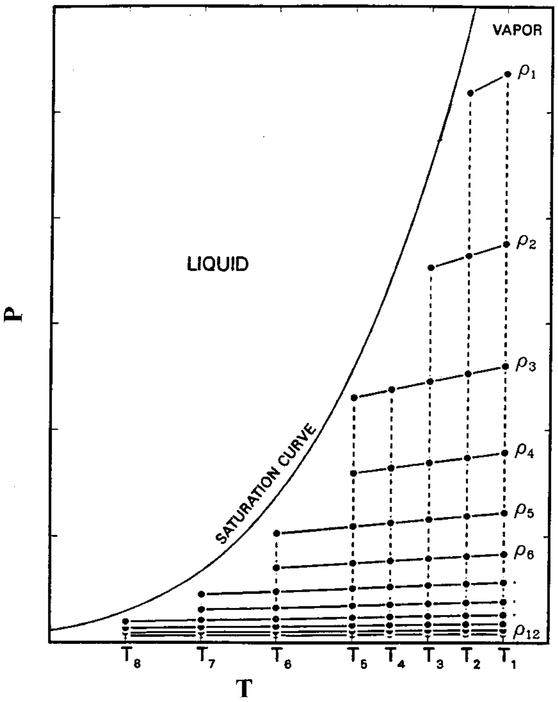

Figure 3. Typical data pattern for the Burnett-isochoric apparatus.

with Ewing and associates feeling that all of the differences were due to adsorption errors in the older $P-V-T$ measurements and discounting the smaller differences above 400 K where their values of $B(T)$ become more negative. On the other side, most $P-V-T$ experimentalists distrust sonic-velocity-based values due to error propagations in eq 1 and further feel that adsorption is only important with polar gases and not with simple hydrocarbons. The latest edition of Dymond and Smith (1980), *The Virial Coefficients of Pure Gases and Mixtures*, was delayed because the credibility of many of the values therein was uncertain.

Experimental Section

Apparatus. Figure 2 is a schematic of the Burnett-isochoric (B-I), $P-V-T$ cell used in these measurements, whereas Figure 3 shows the nature of B-I data, which for one run (one sample) can cover a region of pressures and temperatures with its (1) isochores and (2) Burnett isotherms. These figures are not new but convenient for the reader in understanding the data and error sources. The experimental apparatus is not shown because while inactive for a number of years it remains similar to that described in the publications of Joffrion and Eubank (1988), Eubank et al. (1988), Patel and Eubank (1988). The Burnett cells, V_A and V_B of Figure 2, were refinished and micropolished to a mirror finish. The valves were replaced, and other clean-up duties were performed. The only major changes in the apparatus were those associated with lowering the temperature range, previously 298−498 K. Figure 1 has shown the largest sonic velocity/$P-V-T$ disagreement is at 250 K, the lowest temperature of the sonic velocity measurements. We attempted to lower our low-temperature limit to 250 K but succeeded only to 265 K due to problems with insulation of a large 0.120 m^3 bath. A less viscous silicone oil, Dow Corning 200, was used as the bath fluid, but this lowered our upper temperature limit to 450 K. The top lid of our temperature bath is not airtight due to many feed-throughs and one rotating mixer shaft plus the necessity to allow for the thermal expansion of the silicone oil; at these lower temperatures, water vapor condensed out of the air blanket, on top of the silicone oil inside the bath, to slowly form ice that was then stirred into the silicone oil by the mixer. This problem was solved by bleeding dry nitrogen into the top of the bath. All individual instruments were recalibrated; the helium calibration that followed will be described later. Complete details concerning the apparatus and experimental procedures may be found in Gupta (1996).

Table 1. Cell Constants from Burnett Isothermal Helium Data

	linear fit		surface fit	
T/K	N	$\sigma(N)$	N	$\sigma(N)$
450.0	1.452 003	0.000 095	1.451 950	0.000 036
264.9	1.452 011	0.000 039	1.452 140	0.000 066

Substances. Helium with a 99.9995% purity was supplied by Air Products for calibration purposes. Two forms of butane were used: (1) a large commercial cylinder of 99% purity was used for flushing, and (2) research grade of 99.89% minimum purity was supplied by Matheson Gas Products in lecture bottles as a liquid. The impure butane was used to flush the Burnett cells and connecting lines (Figure 2), followed by evacuation to 0.13 Pa. Because the original charge of the research grade butane was at 3.3 and 1.1 MPa for runs I and II, respectively, multiple flushing with the impure butane resulted in purities approaching that of the research grade or 99.89%. A detailed chemical analysis of the research grade material showed that the main impurities were propane (483 ppm) and isobutane (612 ppm) with no other impurity exceeding 10 ppm. For $B(T)$, propane values are roughly 50% as negative as those of butane over the present range of temperature whereas those of isobutane are roughly 8% less negative. Ideal solution assumptions yield errors of less than 0.03% in $B(T)$ for butane due to these impurities.

Helium Calibration

Helium is the calibration gas of choice because (1) $B(T)$ is weakly positive at ambient temperature causing small deviations from perfect gas behavior even at elevated pressures where the compressibility factor Z is nearly linear with pressure, (2) it is inert, (3) it can be obtained inexpensively in a very pure form, and (4) it provides an excellent test for small leaks in the apparatus—indeed, we have long used mass spectrometers using helium for leak tests.

Table 1 provides the Burnett cell constant $N \equiv [(V_A + V_B)/V_A]$ and the standard deviation σ for helium at 264.9 K and 450 K, the extreme temperatures of this study. Two data reduction schemes were used. The first, labeled linear fit, is essentially a weighted least-squares analysis (Joffrion and Eubank, 1988), whereas surface fit is a nonlinear least-squares analysis using a maximum likelihood program

Table 2. Helium Second Density Virial Coefficients from Isothermal Analysis and Comparison with Literature Values

T/K	B/cm^3 mol^{-1}	reference
450.0	10.14	this work[a]
	10.54	this work[b]
	10.43	Kudchadker (1967)
	11.3	Angus et al. (1977)
350.0	11.08	this work[a]
	11.04	this work[b]
	11.63	Kudchadker (1967)
	11.51	Kerns (1972)
	11.65	Blancett et al. (1970)
	11.7	Angus et al. (1977)
264.9	11.80	this work[a]
	11.67	this work[b]
	11.98	Blancett et al. (1970)

[a] Obtained using linear fit of data. [b] Obtained using maximum-likelihood estimates, same as surface fit.

developed by Embry (1980). As with the butane data to follow, corrections have been made for (1) deviation from the exact isotherm, (2) cell distortions with pressure and, more importantly, temperature (for isochores) and a host of other standard corrections given by Gupta (1996). The weighing factors used in both data reduction procedures involve mostly the standard deviation associated with an air dead weight gauge used for all the pressure measurements. Here, $\sigma(P_i) = P_i \times 10^{-4}$ for $P_i \geq 690$ kPa but $\sigma(P_i) = 69$ Pa for $P_i \leq 690$ kPa. Because weighing factors are proportional to the inverse square of the standard deviation, these weighing factors account for the high relative errors in the higher pressure values and in the high absolute errors in the lower pressure values. It was also assumed that all random errors in the experiments were localized in the pressure measurements, as deviations due to temperature were only a fraction of the pressure deviations on a relative basis (percent deviation). The Burnett cell constants at 264.9 K and at 450 K are nearly identical for the linear fit and are within a combined 2σ for the surface fit. In 35 years of operation, this apparatus has fortuitously had helium N-values independent of temperature. That is, the percent expansion of the primary cell V_A with temperature is essentially the same as that of cell V_B.

Table 2 lists the corresponding values of $B(T)$ for helium at 264.9, 350 and 450 K with comparison to some of the previous measurements, most of which are interpolated values. Fortunately, over this temperature range $B(T)$ decreases gently with increasing temperature. A more detailed comparison with all of the previous values given in Dymond and Smith (1980) shows these new values to be perhaps slightly on the low side but within combined standard deviations of most other determinations.

Butane Results

Run I. Figure 4 illustrates the data points taken in the B-I run I for butane. The apparatus constant N should be the same as the isothermal cell constant U_0

$$U_0 \equiv \lim_{P_i \to 0} (P_i/P_{i+1}) \qquad (3)$$

provided there is no physical adsorption or leaks. Table 3 shows that U_0 is relatively constant with temperature but that the statistically averaged value of 1.481 70 ($\langle\sigma\rangle = 0.000\,318$) is surprisingly very much higher than the statistically averaged value of 1.452 001($\langle\sigma\rangle = 0.000\,073$) for helium. We later reproduced the helium and the butane values (run II, below) with the result that both are highly reproducible, independent of temperature, and very different. Physical adsorption would cause the value for butane to deviate greatly with temperature as the temperature drops below the critical value of 425 K; there should be little adsorption at 425 K and much less at 450 K, so the value of U_0 should be the same as the helium N at those temperatures. Leaks cause great scatter in the sensitive U_0 and are very obvious. Thus we have a result that is expected only when we have changed the associated tubing of Figure 2 or repolished a cell between the helium and butane runs; however, we did nothing here and could switch back-and-forth between helium and butane with each providing reproducible results and virial coefficients close to literature values for both substances. Our colleagues, J. C. Holste and K. R. Hall, called our attention to the fact that the new Burnett valve packing (see Figure 2) that we were using was made of Teflon impregnated with graphite and its pores could swell in the presence of a solvent such as butane. The gas in the primary volume V_A sees nothing but stainless steel as the Burnett expansion valve packing is turned toward the second volume V_B. One would then expect that the effective value of V_B would be larger for butane than for helium, resulting in a butane N-value greater than that of helium. For B-I data, the base B-I isotherm of 450 K is the only temperature at which expansions into V_B are made and so the only opportunity for pore swelling. It can be shown (Gupta, 1996) using adsorption diagnogics and equations (Warowny and Eu-

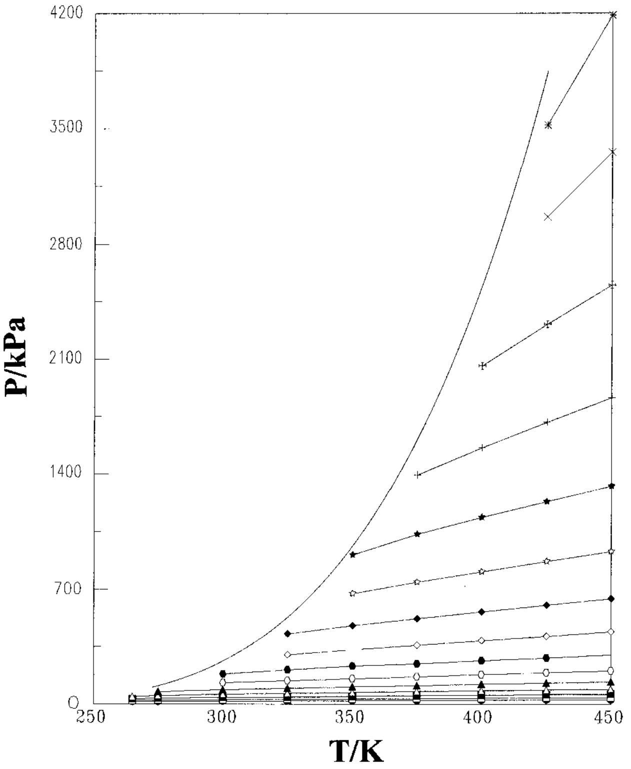

Figure 4. Pressure and temperature measurements of butane (run I).

Table 3. Cell Constant, U_0, Using Run I Surface Fit of Butane[a]

T/K	U_0	$\sigma(U_0)$
450	1.481 79	0.000 24
425	1.481 62	0.000 31
400	1.481 66	0.000 22
375	1.481 71	0.000 89

[a] The average value, $\langle U_0\rangle$ was fixed at 1.481 70 in further analysis with $\langle\sigma\rangle = 0.000\,318$.

Table 4. Experimental Data of the Butane $P-V-T$ Surface in Run I Uncorrected for Adsorption

isochore number	ρ(450 K)/mol dm^{-3}	P/kPa								
		$T = 450$ K	$T = 425$ K	$T = 400$ K	$T = 375$ K	$T = 350$ K	$T = 325$ K	$T = 300$ K	$T = 275$ K	$T = 264.9$ K
14	0.007 67	28.592	27.012	25.391	23.876	22.168	20.517	18.699	16.856	15.580
13	0.011 36	42.211	39.863	37.493	35.210	32.751	30.336	27.764	24.822	22.802
12	0.016 83	62.539	59.042	55.492	52.045	48.350	44.609	40.722	35.942	32.854
11	0.024 94	92.814	87.614	82.295	77.242	71.640	66.042	60.113	52.395	47.202
10	0.036 95	136.884	129.131	121.328	113.544	105.403	97.028	87.983	74.933	
9	0.054 76	201.774	190.228	178.568	166.833	154.823	142.177	127.925		
8	0.081 13	296.621	279.310	261.851	244.184	229.415	206.699	182.957		
7	0.120 21	434.909	408.802	382.515	355.826	328.095	297.997			
6	0.178 11	633.706	594.036	554.336	513.719	471.093	420.988			
5	0.263 91	916.239	856.339	795.062	732.014	664.499				
4	0.391 03	1309.248	1216.179	1120.675	1021.205	896.646				
3	0.579 38	1838.257	1691.705	1539.737	1376.027					
2	0.858 45	2513.669	2277.755	2029.787						
1	1.271 93	3308.022	2920.029							

Table 5. Density Second Virial Coefficients, B, of Butane at Different Temperatures from Run I Using (I) Surface Fit and (II) Fixed U_0

	U_0 from surface fit		$U_0 = 1.481$ 70 (fixed)	
T/K	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}
450	−282.45	2.14	−281.5	0.22
425	−321.09	1.42	−321.5	0.49
400	−368.75	1.65	−369.0	0.51
375	−430.9	17.3	−426.5	2.79

bank, 1995) that the densities and virial coefficients of the butane are not affected as long as the effect is linear with density *on the base isotherm*; however, one must use the U_0 for butane (Table 3) as N in reducing the butane data and the helium N in reducing the helium data. However, such a large shift in the apparatus constant provides $f_B = 0.061$ 65, where f_B is the fraction of molecules adsorbed. However, any value of this parameter greater than 0.01 will cause extreme curvature in Figure 6, where the 450 K isotherm is straight except for the lowest pressure datum. Thus, we conclude that the apparatus constant shift between helium and butane is not caused by an adsorption-type mechanism but rather by an increase of the effective volume of V_B due to pore swelling. Obviously, the virial coefficients and densities are not changed by different apparatus constants—otherwise we could not compare data from different laboratories or with measurements from a simple Beattie cell where there is no secondary volume. Thus, we will not term this phenomena adsorption in the remainder of this article so as not to confuse it with the physical adsorption that we see below for butane molecules onto the stainless steel wall of V_A along the isochores that go below 375 K. The two phenomena are clearly very different; the first we have not seen before but requires no correction of densities and virial coefficients, while for the second we have much experience in the diagnosis and correction of physical adsorption in gases well below the critical temperature.

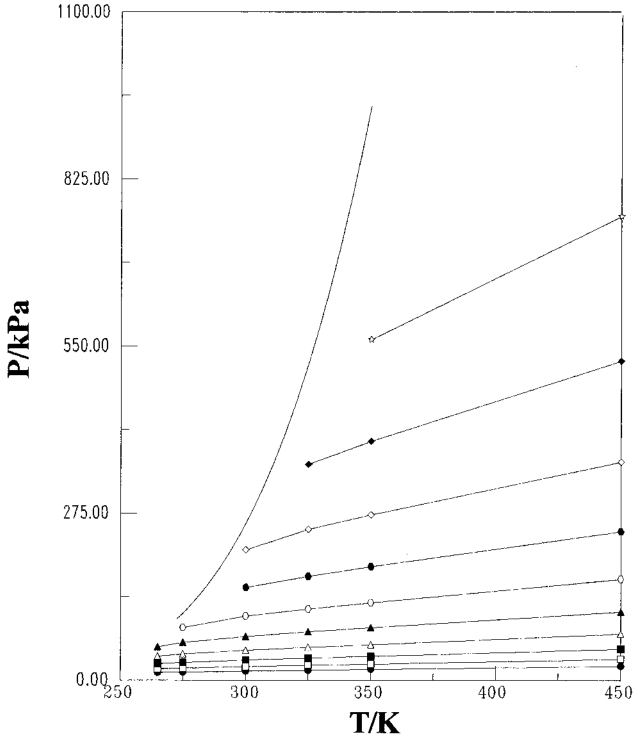

Figure 5. Pressure and temperature measurements of butane (run II).

Table 6. Density Third Virial Coefficients, C, of Butane at Different Temperatures from Run I Using (I) Surface Fit and (II) Fixed U_0

	U_0 from surface fit		$U_0 = 1.481$ 70 (fixed)	
T/K	C/cm^6 mol^{-2}	$\sigma(C)$/cm^6 mol^{-2}	C/cm^6 mol^{-2}	$\sigma(C)$/cm^6 mol^{-2}
450	335 55	1403	329 74	149
425	358 59	856	360 73	346
400	370 77	1383	372 87	512
375	349 95	27533	252 58	4054

Table 4 contains the *raw data* for run I uncorrected for adsorption. It should be noted that the data below 375 K were taken only after a delay of over two months due to cooler malfunctions. *These data are suspect due to the long term accumulation effect of undetectable leaks.* The data above 375 K do not require correction for adsorption and so are used in Tables 5 and 6 to report second and third virial coefficients, respectively. These tables show virial coefficients obtained with either (1) the floating U_0 corresponding to Table 3 or (2) the statistically averaged value of $U_0 = 1.481$ 70 as a fixed parameter. In Burnett or B-I data analysis, it is useful to think of U_0 as the first virial coefficient, even though that value is actually unity. As seen in Tables 5 and 6, $B(T)$ is very sensitive to U_0 and $C(T)$, in turn, is very sensitive to $B(T)$. There is good agreement between the two procedures except at 375 K where the more negative $B(T)$ of the first method requires a very positive $C(T)$ to compensate to yield measured densities from the virial EoS. Fixing U_0, the lead parameter, causes lower standard deviations in $B(T)$ and $C(T)$. All values in these two tables were obtained from the maximum likelihood program developed by Embry (1980).

Run II. Figure 5 shows that this set of B-I measurements focused on the lower temperature isotherms of 350, 325, 300, 275, and 265 K connected to the supercritical base isotherm of 450 K. Table 7 contains the *raw data* for run

Table 7. Experimental Data of the Butane $P-V-T$ Surface in Run II Uncorrected for Adsorption

isochore number	ρ(450 K)/mol dm^{-3}	P/kPa					
		T = 450 K	T = 350 K	T = 325 K	T = 300 K	T = 275 K	T = 264.9 K
11	0.006 32	23.541	18.313	16.830	15.279	13.600	12.734
10	0.009 37	34.929	27.120	25.008	22.735	20.100	18.843
9	0.013 88	51.706	40.103	36.872	33.514	29.452	27.449
8	0.020 57	76.495	59.173	54.566	49.552	43.309	39.681
7	0.030 48	113.024	87.325	80.286	72.716	62.645	55.372
6	0.045 16	166.806	128.177	117.796	106.214	87.347	
5	0.066 90	245.599	187.716	172.004	153.468		
4	0.099 14	360.474	273.367	249.239	215.382		
3	0.146 89	526.921	394.972	356.494			
2	0.217 64	765.379	562.592				
1	0.322 48	1100.826	781.653				

Table 8. Data of the Butane $P-V-T$ Surface in Run II Corrected for Adsorption

isochore number	ρ(450 K)/mol dm^{-3}	P/kPa					
		T = 450 K	T = 350 K	T = 325 K	T = 300 K	T = 275 K	T = 264.9 K
11	0.006 32	23.614	18.346	17.022	15.699	14.377	13.848
10	0.009 37	34.958	27.141	25.177	23.212	21.245	20.458
9	0.013 88	51.730	40.125	37.205	34.283	31.354	30.181
8	0.020 57	76.503	59.255	54.910	50.554	46.183	44.429
7	0.030 48	113.032	87.363	80.882	74.375	67.828	65.192
6	0.045 16	166.777	128.494	118.796	109.034	99.181	
5	0.066 9	245.579	188.306	173.722	158.993		
4	0.099 14	360.537	274.456	252.376	229.953		
3	0.146 89	526.979	396.721	362.946			
2	0.217 64	765.273	566.203				
1	0.322 48	1100.800					

Table 9. Second Virial Coefficients of Butane Using Run II with U_0 = 1.481 70 (Fixed) without Adsorption Correction

T/K	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}	T/K	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}
450	−286.8	1.36	300	−1283	50.6
350	−512	193	275	−3008	212
325	−666	3.74	264.9	−4631	229

Table 10. Second Virial Coefficients of Butane Using Run II with U_0 = 1.481 70 (Fixed) and Corrected for Adsorption

T/K	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}	T/K	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}
450.0	−286.8	1.36	300[a]	−706.0	0.28
350.0	−494.5	1.54	275[a]	−871.0	1.52
325.0	−586.8	0.97	264.9[a]	−957.6	3.37

[a] Indicates that fit of data was limited to B only, and in other cases third virial coefficient, C, was also obtained as a fitted parameter.

Table 11. Third Virial Coefficients of Butane Using Run II with U_0 = 1.481 70 (Fixed) and Corrected for Adsorption

T/K	C/cm^6 mol^{-2}	$\sigma(C)$/cm^6 mol^{-2}	T/K	C/cm^6 mol^{-2}	$\sigma(C)$/cm^6 mol^{-2}
450.0	46 619	4556	300[a]		
350.0	32 147	3840	275[a]		
325.0	26 634	5048	264.9[a]		

[a] Indicates that fit of data was limited to B only, and only at temperatures above 325 K in Run II third virial coefficient, C, was obtained.

II uncorrected for adsorption, whereas Table 8 contains the corresponding values corrected for adsorption. A smoothed version (even increments of pressure) of Table 4 (run I) to 375 K and also of Table 8 (run II) is available from the authors in SI units or in Gupta (1996) with pressures in psia. Table 9 has the second virial coefficients uncorrected for adsorption, whereas Table 10 has the corresponding corrected values of $B(T)$. Corrected third virial coefficients are in Table 11. Comparison of Tables 9 and 10 shows that adsorption, a systematic error, cannot be discounted by a low standard deviation; unless the adsorption is especially slow, a reproducible equilibrium will be achieved with false virial coefficients as a result.

Treatment for Adsorption. The run I values of U_0 = 1.481 70 and $\langle\sigma\rangle$ = 0.000 318 were used throughout the run II analysis. The isothermal analysis at 450 K provides the density of each isochore (cell V_A). Figure 6 shows the sensitive $[(Z-1)/\rho]$ *vs* ρ graph, where the compressibility factor Z is $(P/\rho RT)$ and ρ is the molar density. When even a trace of adsorption is present, the $[(Z-1)/\rho]$ is divergent as the pressure approaches zero. The scatter in the measured pressures, discussed previously, will be amplified on the graph, but Figure 6 shows every isotherm bending downward, a telltale sign of adsorption that also leads to too negative values of $B(T)$.

The following procedure was developed for adsorption correction of the B-I data of run II:

(i) Burnett isothermal analysis was done at each temperature to provide initial densities, $B(T)$ and $C(T)$.

(ii) The densities at each isotherm were compared with the density values obtained at 450 K (same isochore).

(iii) Changes in pressure, ΔP_i, corresponding to the density difference of ii were found from

$$(\Delta P)_i = (\partial P/\partial\rho)_T(\Delta\rho)_i; \quad P = \rho RT[1 + B\rho + C\rho^2];$$
$$(\partial P/\partial\rho)_T = RT[1 + 2B\rho + 3C\rho^2] \quad (4)$$

with each Δ being the corrected value less the uncorrected. The derivative of eq 4 is estimated from the initial values of B and C.

(iv) Burnett isothermal analysis was repeated for each isothermal with the corrected pressures to obtain updates of the densities, B and C.

(v) Steps ii to iv were repeated to convergence.

(vi) Linearity of the $[(Z-1)/\rho]$ *vs* ρ graph was checked as shown by Figure 7.

The initial values of $(\Delta\rho)_i$ are equivalent to the moles of butane adsorbed at various measured pressures and tem-

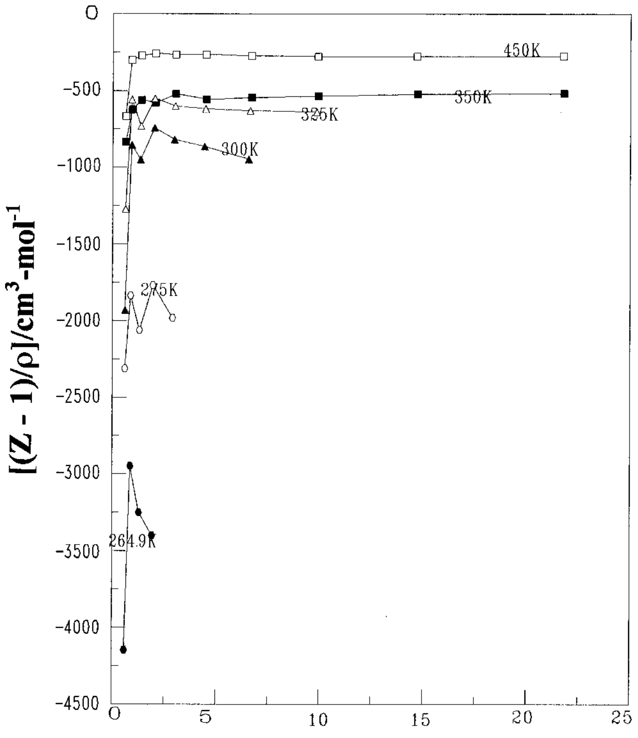

Figure 6. $(Z - 1)/\rho$ *vs* ρ plot of butane when uncorrected for adsorption.

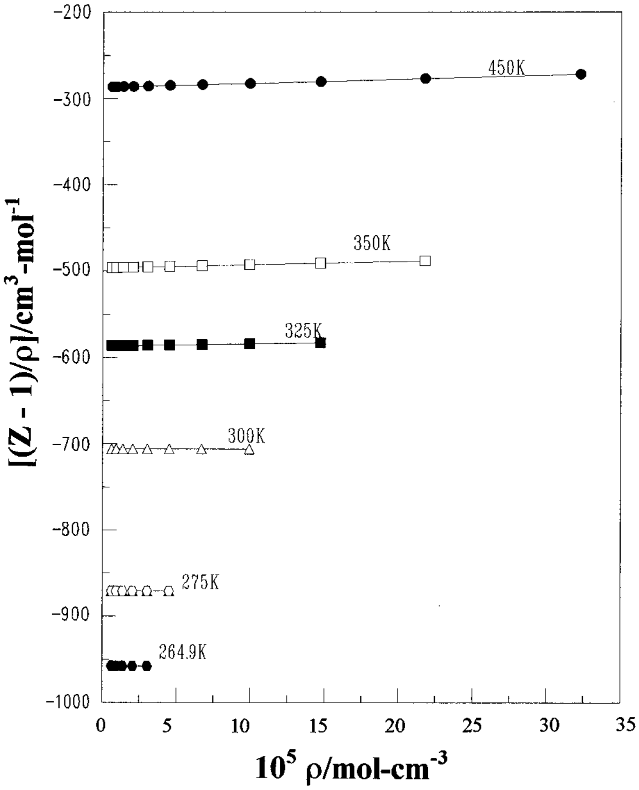

Figure 7. $(Z - 1)/\rho$ *vs* ρ plot of butane when corrected for adsorption.

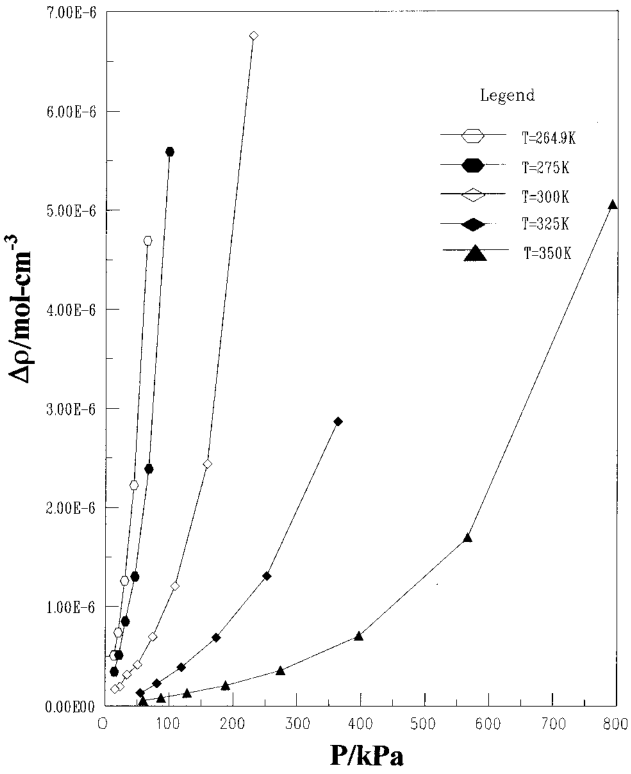

Figure 8. Amount of butane adsorbed, in mol cm^{-3}, along isotherms in the present data.

Table 12. Adsorption Constants k_1 and k_2 in BET Model for Butane Adsorbed on a Stainless Steel Surface for Run II

T/K	10^6 k_1/ mol cm^{-3}	k_2	T/K	10^6 k_1/ mol cm^{-3}	k_2[a]
265	2.39377	−0.5847	325	1.2943	0
275	2.6149	−0.6796	350	0.9541	0
300	1.669	−0.901			

[a] Simple adsorption model for T = 325 K and 350 K was assumed.

Table 13. Comparison at 450 K using Maximum Likelihood for Runs I and II

run no.	pressure range used in analysis (kPa)	U_0	B(450 K)/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}
run I	0−3500	1.481 79[a]	−282.45	2.1
run I	0−1400	1.481 70[b]	−284.8	2.4
run II	0−1400	1.481 76[a]	−287.5	7.0
run II	0−1400	1.481 70[b]	−286.8	1.4

[a] These values of U_0 are obtained as maximum likelihood estimates from N, B, and C analysis. [b] U_0 was fixed at these values of cell constants and used in the maximum likelihood program.

peratures and are shown in Figure 8 to resemble Brunauer, Emmett, and Teller (B−E−T) type adsorption isotherms (Oscik, 1982). Constants k_1 and k_2 for the B−E−T model

$$(m/V) = \{k_1P/(P^\sigma - P)[1 + (k_2P/P^\sigma)]\} \qquad (5)$$

are given in Table 12. In eq 5, P^σ is the vapor pressure and m is the moles adsorbed per total volume V of gas. Simple BET adsorption ($k_2 = 0$) is sufficient above about 300 K.

Recommended Values of the Virial Coefficients. First, we were concerned that our values for $B(T)$ at 450 K were not in better agreement; run I was −281.5 ($\sigma = 0.22$ cm^3·mol^{-1}) with U_0 fixed at 1.481 70, whereas run II has −286.8 ($\sigma = 1.36$ cm^3·mol^{-1}). A major difference between the two runs is that the first extends to a pressure of 3.3 MPa whereas the second goes only to 1.1 MPa. It is well-known that pressure ranging can affect virial coefficients from numerical data reduction routines although this is theoretically not acceptable. Table 13 shows that data ranging run I to the same pressures as those of run II does indeed raise $B(T)$ to −284.8 ($\sigma = 2.4$ cm^3·mol^{-1}), but the

Table 14. Recommended Density Second Virial Coefficients and Density Third Virial Coefficients of Butane from This Study

T/K	B/cm^3 mol^{-1}	$\sigma(B)$/cm^3 mol^{-1}	C/cm^6 mol^{-2}	$\sigma(C)$/cm^6 mol^{-2}
450.0	−281.5	0.22	32 794	149
425.0	−321.5	0.49	36 073	346
400.0	−369.0	0.51	37 287	512
375.0	−426.5	2.79	34 995	27533
350.0	−494.5	1.54	32 147	3840
325.0	−586.8	0.97	26 634	5048
300[a]	−706.0	0.28		
275[a]	−871.0	1.52		
264.9[a]	−957.6	3.37		

[a] Indicates that fit of data was limited to B only, and in other cases third virial coefficient, C, was also obtained as a fitted parameter.

Table 15. Constants for Fit of Eq 6 To Calculate Density Second and Density Third Virial Coefficients at Other Temperatures

B_0/cm^3 mol^{-1}	552.543	C_0/cm^6 mol^{-2}	−172 446
B_1/K cm^3 mol^{-1}	−604 946.8	C_1/K cm^6 mol^{-2}	1.656×10^8
B_2/K^2 cm^3 mol^{-1}	1.7349×10^8	C_2/K^2 cm^6 mol^{-2}	-3.285×10^{10}
B_3/K^3 cm^3 mol^{-1}	-3.1575×10^{10}		

standard deviation also increases over 10-fold. Because even the worst agreement (first sentence above) is near 3σ combined deviation, we chose to simply take the less negative value of run I because of its low σ. Likewise, we have selected $C(T)$ at 450 K from run I in Table 14. As there are no other overlapping temperatures, other recommended values of $B(T)$ and $C(T)$ in Table 14 are more easily selected. However, at 375 K, we believe that $C(T)$ of run I in Table 6 is not in line with the values at the higher temperatures for the fixed U_0 and have selected instead the higher value from the surface fit with its high σ. We do not have a good reason for this except that it puts our recommended $C(T)$s in line while accepting a too-large σ that well covers our selection. It will be shown below that a Lennard-Jones fluid forecasts a maximum in $C(T)$ near 375 K with values in rough agreement with our own. For use at other than experimental temperatures, our recommended values of $B(T)$ and $C(T)$ have been fit to a power series in inverse temperature of the form

$$B = B_0 + (B_1/T) + (B_2/T^2) + (B_3/T^3) \qquad (6)$$

where the B_js are empirical constants without physical meaning. Values for these B_js and the corresponding C_js may be found in Table 15.

Comparison with Other Values

Here we compare our recommended virial coefficients, corrected for adsorption, with corresponding literature values and, for $C(T)$, molecular-based model values. Figure 9 is such a comparison for $B(T)$ with more recent literature—it does not include older $P-V-T$ measurements; a complete, detailed comparison for $B(T)$ is given by Gupta (1996). Both Dymond et al. (1986) and NBS (Haynes and Goodwin, 1982) are recommended values from a correlation of literature measurements. Ewing et al. (1988) was discussed in the Introduction, whereas Ababio et al. (1994) are new, independent, $P-V-T$ measurements. Table 16 is a comparison with Dymond et al. (1986) representing the older $P-V-T$ measurements; our values have been interpolated and slightly extrapolated at 250 K and 460 K. The agreement is very good at temperatures above about 375 K, where we found little adsorption errors in our measurements. Below 375 K, the values selected by Dymond begin to diverge more negatively from our own, reflecting, we believe, uncorrected adsorption errors in the older density measurements. Our comparison with the NBS values, Table 16, follows a similar trend except that the agreement is so good at the higher temperatures so as to be at least partially fortuitous whereas at lower temperatures the agreement is not quite as good as that with Dymond (i.e., the NBS values are somewhat more negative). Table 16 shows the comparison with the sonic-velocity-based values of Ewing et al. (1988). Ewing is less negative at the lower temperatures and more negative at the higher temperatures with a cross-point near 345 K, again not far from where adsorption becomes important in our data. Because of its complexity, we will discuss why we have these differences, which while not in excess of about 25 cm^3/mol are definitely systematic, in the next section. Table 16 compares our $B(T)$ with those recommended by Tsonopoulous et al. (1989) on the basis of both sonic and $P-V-T$ measurements at the lower temperatures. While the agreement is reasonable, it appears that the authors should have given more weight to Ewing et al. (1988).

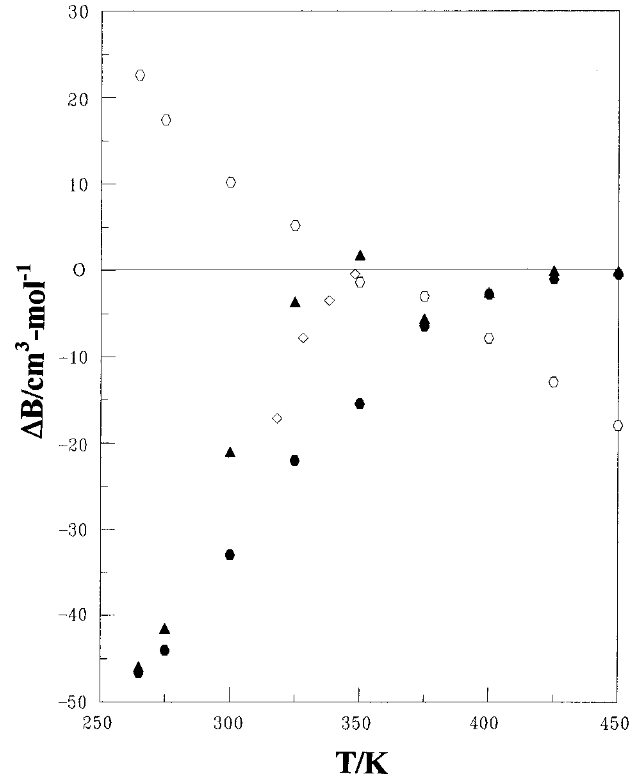

Figure 9. Deviations of density second virial coefficients compared with literature for butane: (▲) Dymond et al. (1982), (○) Ewing et al. (1988), (●) Haynes and Goodwin (1982), and (◇) Ababio (1994).

Third virial coefficients of butane are more sparse and, as usual, of more questionable quality as they are difficult to measure within ±5%. Figure 10 contains all of the measurements available to our knowledge. Our agreement with Ewing is not nearly as good as it appears in Figure 10 considering the scale of the ordinate. Further, the Ewing measurements only extend from 250 to 320 K, so Figure 10 includes many values extrapolated to higher temperature with their equation based upon a square-well potential. Figure 11 shows a comparison of our measured $C(T)$ with values determined by a Lennard-Jones (12−6) potential whose constants, $(\epsilon/\kappa) = 317$ K and $\sigma = 0.577$ nm, were determined from our measured $B(T)$. The L-J results for $C(T)$ assisted in our selection of the recommended $C(T)$

Table 16. Comparison of Density Second Virial Coefficients, *B*, of Butane from This Study with Recommended Values by the National Bureau of Standards (Haynes and Goodwin, 1982; Dymond et al., 1986; Tsonopolous et al., 1989) and with Values Derived from Speed-of-Sound by Ewing et al. (1988)

T/K	B/cm^3 mol^{-1} (Haynes and Goodwin, 1982)	B/cm^3 mol^{-1} (Dymond et al., 1986)	B/cm^3 mol^{-1} (Tsonopolous et al., 1986)	B/cm^3 mol^{-1} (Ewing et al., 1988)	B/(cm^3/g mol^{-1}) (this study)
250		−1170			−1112.2
260		−1050			−1004.2
264.9	−1004.2			−935.0	−957.6
270		−950	−925		−912.3
275	−915.0			−853.6	−871.0
280		−862	−845		−833.5
290		−788	−780		−765.2
300	−738.9	−722		−695.8	−706.0
320		−620			−607.3
325	−608.8			−581.6	−586.8
340		−535			−529.3
350	−509.9			−495.8	−494.5
360		−472			−466.0
375	−432.9			−429.5	−426.5
380		−417			−413.4
400	−371.8	−370		−376.9	−369.0
420		−332			−330.5
425	−322.5			−334.4	−321.5
440		−299			−296.9
450	−281.9			−299.5	−281.5
460		−270			−267.0

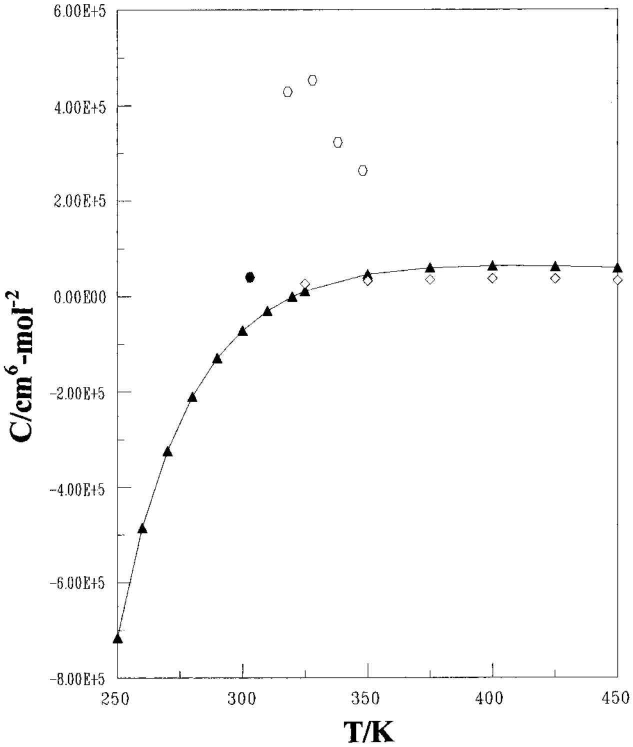

Figure 10. Comparison of the third virial coefficients of butane: (−▲−) Ewing et al. (1988); (○) Ababio (1994); (●) Scott and Dunlap (1962); (◇) this work.

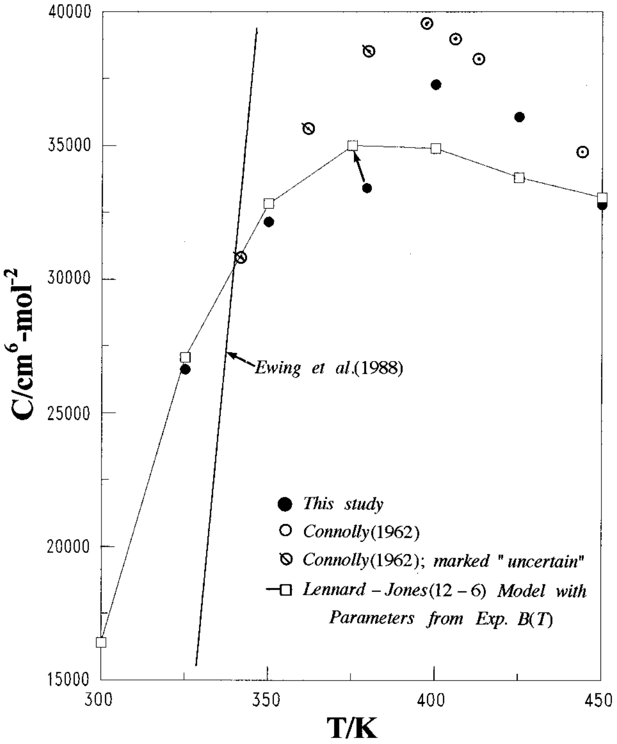

Figure 11. Comparison of experimental third density virial coefficients from this study with Lennard-Jones potential model values from fit of our experiment second virial coefficients and with the literature values of Connolly (1962) and of Ewing et al. (1988).

from the surface fit value of run I in Table 6, as described previously.

Figure 11 shows our agreement with Connolly (1962) to be excellent. Although Connolly marked his three low-temperature values as *uncertain*, it now appears that they were the best values in the literature for the past 37 years. The agreement with a Lennard-Jones (12−6) model with parameters from our $B(T)$ data shows the consistency between our $B(T)$ and $C(T)$ results. The nearly vertical line through the data of Figure 11 is a slight extrapolation of the Ewing et al. (1988) equation for $C(T)$. At their highest experimental temperature of 320 K, $C(T)$ is 2000 cm^6/mol^2 whereas our value would be about 25 500, based upon a 5° extrapolation supported also by the Lennard-Jones model values. As discussed by Ewing et al. (1988), further extrapolation of their equation for $C(T)$ shows a maximum of about 63 000 near 400 K, but such extrapolation is less reliable as compared to their equation for $B(T)$: "...suggest that B may be extrapolated up to the critical temperature of butane (425 K) with useful accuracy. Extrapolation of C is expected to be much less reliable; ...". Nevertheless, there are major problems with the $C(T)$ values of Ewing et al. (1988), even within 250−320 K. For example, at 300 K, they have −71 000 whereas the Lennard-Jones value of Figure 11 is about +17 500. We understand that once C goes negative for decreasing T, the slope (dC/dT) is very steep, but this difference is far too much. Extrapolation of our Lennard-Jones model yields $C(T)$ of $-24\,400(-398\,000$ from Ewing) at 265 K, our lowest T for $B(T)$, and $C(T)$ of $-60\,200(-716\,000$ from Ewing) at 250 K, Ewing's lowest T. Further, for a L-J fluid, $(k_BT_c/\epsilon) \cong 1.30$ (Hirschfelder et al., 1954) and $b_0 \equiv (2\pi\sigma^3/3) \cong 0.2146(RT_c/P_c)$ from the well-known fact that $(B_cP_c/RT_c) \cong (-0.34 \pm 0.01)$ for all fluids at their critical temperature. For butane B_c (425 K) $= (-316.5 \pm 9.3)$, in agreement with our better measured value of -321.5; nevertheless, this procedure provides universal curves for (BP_c/RT_c) and $C(P_c/RT_c)^2$ *vs* (T/T_c) roughly valid for nonpolar compounds. For $C(T)$, the universal curve shows a maximum of 23 800 at 382 K; at 265 K, it is -7800 but (dC/dT) is about 400 cm^6/mol^2·K.

Discussion

We believe that the recommended values in Table 14 are *precise* to roughly $\pm 2\sigma$, but as usual, *accuracy*, which includes systematic errors, is another matter. Comparison of $B(T)$ of Table 9, run II uncorrected for adsorption, with the recommended values shows that the adsorption effect was only a few cm^3/mol at the higher temperatures but almost 500% at 264.9 K! Of course, Table 9 is based on Burnett isothermal analysis of B-I data. A B-I analysis, complete surface fit with fixed $U_0 = 1.481\,70$, yields results similar to previous $P-V-T$ studies not corrected for adsorption with maximum corrections in $B(T)$ of 50−70 cm^3/mol at 264.9 K. In previous adsorption correction work (Joffrion and Eubank, 1988; Eubank et al., 1988; Patel and Eubank, 1988 and references within), we have gained confidence that we can successfully correct for 90−95% of the adsorption errors. Here that would be 4 to 7 cm^3/mol uncorrected for at 264.9 K decreasing to less than 0.2 cm^3/mol at 450 K. Assuming our dominating systematic error is indeed adsorption, then we can combine it with random errors of roughly 2σ to estimate the accuracy for the recommended $B(T)$ of Table 14 as ranging from about ±14 cm^3/mol (we keep the ± as adsorption corrections can be either underestimated or overestimated) at 264.9 K to ±4.5 cm^3/mol at 350 K to ±1 cm^3/mol at 450 K.

Thus our data is not of sufficient quality at the lower temperatures to challenge Ewing's more positive values of $B(T)$. Indeed, considering all the uncertainties in the two measurements, our values overlap within uncertainty error bands from 264.9 to 320 K, the latter being the upper limit of Ewing's measurements. In random errors, Ewing's standard deviation was 0.48 cm^3/mol (about 0.04%) in the sonic second virial coefficient β_a. However, Eubank et al. (1994) have shown that error propagation factors of 100 times at 250 K to 30-fold at 420 K should exist between β_a and $B(T)$ for butane even when the correct temperature form of $B(T)$ is used in reducing the sound speed data. That study also showed that Ewing's choice of a square-well potential model

$$B(T) = a - be^{c/T} \tag{7}$$

came very close to fulfilling that requirement. However, the study by Eubank et al. (1994) was simulating a case for butane where sound speeds were measured from 250 to 420 K, not the more narrow range of 250−320 K of Ewing's experiments. We did not study the effect of temperature range upon propagation factors, but that should be done. It is well documented (see van Dael (1975), for example) in the sound speed literature that eq 1 should not be used for the $\beta_a(T) \rightarrow B(T)$ transformation without the former data being of a "wide range" of temperature. The problem is compounded below the critical temperature as the second term on the right-hand side of eq 1 grows faster than the first term and also the third term faster than the second with decreasing temperature. In the case of butane at 250 K with Ewing's values, the first term (B) is -1081.46, the second term is 297.35, and the third term is -60.74; these add to yield $(\beta_a/2) = -844.85$. At 425 K, the corresponding values are -334.43, 44.87, and -4.77. Ewing et al. (1988) argue convincingly that the contributions from these derivative terms are less for butane than for a monatomic gas where γ is considerably higher.

At the higher temperatures of this investigation that are above Ewing's highest measured temperature of 320 K, the situation is different. Near the critical at 425 K, for example, we have $B(T)$ as -321.5 ± 1.5 whereas NBS has -322.5, Dymond et al. (1986) have -323.2, Beattie and Stockmayer (1942) have -325.6, Bottomley and Spurling (1964) have -334, Bottomley and Nairn (1977) have -309, and Connolly (1962) has -323.2. Indeed, we agree with Connolly's measurements from 344.26 to 444.26 K with an average deviation of 1.1 cm^3/mol and a maximum deviation of 2.3 at 344.26 K. Thus, Ewing's value at 425 K of -334.4 is too negative by about 13 units; at 450 K, the difference is 18 units. While extrapolating a square-well equation this far above the highest experimental temperature of 320 K is questionable, it does not reflect well upon the equation in general. Indeed, all of our recommended values of $B(T)$ can be fit within a few cm^3/mol by eq 7 with $a = 263.86$, $b = 172.00$, and $c = 519.29$. Alternately, we can fix $a = 165.4$ to match Ewing's value and reproduce our $B(T)$ at 264.9 K and 450 K with $b = 120.23$ (Ewing, 135.42) and $c = 590.84$ (555). However, eq 7 then is as much as 10 units too negative in our middle range of temperature. Regardless of the temperature form used, there is a natural, mathematical tendency to see a teeter-totter effect in reducing $\beta_a(T) \rightarrow B(T)$; that is, it is easy to be high on one end and low on the other—mathematically, it is easier to measure B than (dB/dT). In the previous section, we showed that Ewing's $C(T)$ swings from being much too low below 325 K to being much too high above about 350 K. Our experience is that $C(T)$ always compensates $B(T)$—that is, when $B(T)$ is slightly too high, your $C(T)$ will be much too low and vice versa. It is no coincidence that Ewing's B crosses our measurements at the same temperature as the C's cross. We believe that there is a high probability that this effect has slightly tilted Ewing's results for $B(T)$; the results are still reasonable and must be seriously considered for their temperature range, 250−320 K, where adsorption is present in $P-V-T$ measurements. We further are not implying that this effect is present in similar results from Ewing's laboratory for measurements on other compounds—each case must be examined independently. When all the measurements are supercritical, as in the case of methane (Trusler and Zarari, 1992, 1995) for 275−375 K, the derivative terms in eq 1 are small so there should be little problem. For temperatures well below critical, the sonic procedures still give preferred results over $P-V-T$ measurements *without* diagnosis and correction for adsorption.

Conclusions

Densities and second and third virial coefficients have been measured for butane from 264.9 to 450 K in a $P-V-T$ apparatus designed for subcritical gases and with diagnosis and correction for adsorption. Significant adsorption was found below about 350 K. That adsorption can cause serious errors in $P-V-T$ data for hydrocarbons at temperatures below about 80% of critical has been proven; virial coefficients are especially sensitive. Above this temperature, careful $P-V-T$ measurements are still to be preferred although the large amount of time and money required does not bode well for this *old method* in the future. Major experimental improvements are now rare for a method used by many for many years.

Rapid improvements in the precision of other techniques, such as the sonic velocity experiment, where adsorption is not a major problem, make such methods preferred at temperatures below about 80% of critical. However, these *indirect methods* are not trusted by many for densities and density virial coefficients due to the complicated data reduction required by the connecting thermodynamic identities being differential equations. Eubank et al. (1994) proved via independent simulation that highly accurate second virial coefficients can result from sound speeds, but care must be taken due to high error propagation. Here we have shown that such measurements should be performed over wider temperature ranges. Specifically, we suggest 150−200°; data reduction over the lower 70° range, for example, could then be compared to that using all of the data. The third density virial coefficients for butane from sound speeds (Ewing et al., 1988) have been shown to be unreliable over the entire temperature range (250−320 K), but, again, this situation may improve by sonic measurements over a wider temperature range.

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Literature Cited

Ababio, B. D.; McElroy, P. J.; Willamson, A. G. Virial Coefficients of Butane from Pressure Measurements Only. *Fluid Phase Equilib.* **1994**, *95*, 329−339.

Angus, S.; de Reuck, K. M.; McCarty, R. D. *International Thermodynamic Tables of the Fluid State: Helium-4*; Pergamon Press: Oxford, 1977.

Beattie, J. A.; Stockmayer, W. H. The Second Virial Coefficient for Gas Mixtures. *J. Chem. Phys.* **1942**, *10*, 473−476.

Blancett, A. L.; Hall, K. R.; Canfeild, F. B. Isotherms for the He-Ar System at 50 °C, 0 °C, −50 °C up to 700 ATM. *Physica* **1970**, *47*, 75−91.

Bottomley, G. A.; Spurling, T. H. Measurements of the Temperature Variations of Virial Coefficients. *Aust. J. Chem.* **1964**, *17*, 501−509.

Bottomley, G. A.; Nairn, D. B. Second Virial Coefficients at 300−500 K for Butane, Tetramethylsilane and Freon 114. *Aust. J. Chem.* **1977**, *30* (8), 1645−1653.

Connolly, J. F. Ideality of Butane:Isobutane Solutions. *J. Phys. Chem.* **1962**, *66*, 1082−1086.

Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon Press: Oxford, 1980.

Dymond, J. H.; Cholinski, J. A.; Szafranski, A.; Wyrzykowska-Stankiewicz, D. Second Virial Coefficients for n-Alkanes; Recommendations and Predictions. *Fluid Phase Equilib.* **1986**, *27*, 1−13.

Embry, D. L. *Analysis of Burnett-Isochoric Data*; M.S. Thesis in Chemical Engineering, Texas A&M University College Station, TX, 1980.

Eubank, P. T.; Joffrion, L. L.; Patel, M. R.; Warowny, W. Experimental Densities and Virial Coefficients for Steam from 348 to 498 K with Correction for Adsorption Effects. *J. Chem. Thermodyn.* **1988**, *20*, 1009−1034.

Eubank, P. T.; Chao, Y.-P.; Van Peursem, D.; Gupta, D. Simulation and Propagation of Random and Systematic Errors in Thermophysical Experiments. *AIChE J.* **1994**, *40* (9), 1580−1593.

Ewing, M. B.; Goodwin, A. R. H.; McGlashan, M. L.; Trusler, J. P. M. Thermophysical Properties of Alkanes from Speeds of Sound Determined Using a Spherical Resonator. Part II. Butane. *J. Chem. Thermodyn.* **1988**, *20*, 243−256.

Gupta, D. Simulation and Propagation of Random and Systematic Errors in Thermophysical Experiments. Ph.D. Dissertation in Chemical Engineering, Texas A&M University, College Station, TX, 1996.

Haynes, W. M.; Goodwin, R. D. *NBS Monograph 169: Thermophysical Properties of Normal Butane from 135 to 700 K at Pressures to 70 MPa*; U.S. Department of Commerce, National Bureau of Standards: Boulder, CO, 1982.

Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.

Joffrion, L. L.; Eubank, P. T. *P*−*V*−*T* Data and Virial Coefficients for Gaseous Methane-Water Mixtures with Correction for Adsorption Effects. *Fluid Phase Equilib.* **1988**, *43*, 263−294.

Kerns, W. J. Pressure-Volume-Temperature Relationships of Cyclohexane Vapor. Ph.D. Dissertation in Chemical Engineering Texas A&M University, College Station, TX, 1972.

Kudchadker, A. P. Pressure-Volume-Temperature Relationships of Methanol Gas. Ph.D. Dissertation in Chemical Engineering, Texas A&M University, College Station, TX, 1967.

Oscik, J. *Adsorption*; Ellis Horwood Limited: Chichester, England, 1982.

Patel, M. R.; Eubank, P. T. Experimental Densities and Derived Thermodynamic Properties for Carbon-Dioxide-Water Mixtures. *J. Chem. Eng. Data* **1988**, *33*, 185−193.

Preston-Thomas, H. International Practical Temperature Scale of 1990. *Metrologica* **1990**, *27*, 3−10.

Scott, R. L.; Dunlap, R. D. On the Determination of Second Virial Coefficients. *J. Phys. Chem.* **1962**, *66*, 639-640.

Trusler, J. P. M.; Zarari, M. The Speed of Sound and Derived Thermodynamic Properties of Methane at Temperatures between 275 K and 375 K and Pressures up to 10 MPa. *J. Chem. Thermodyn.* **1992**, *24*, 973−991; *Ibid* **1995**, *27*, 771−778.

Tsonopoulos, C.; Dymond, J. H.; Szafranski, A. M. Second Virial Coefficients of Normal Alkanes, Linear 1-Alkanols and Their Binaries. *Pure Appl. Chem.* **1989**, *61* (8), 1387−1394.

van Dael, W. Thermodynamic Properties and the Velocity of Sound. *Experimental Thermodynamics*; Le Neidre, B.; Vodar, B., Eds.; Butterworths: London, 1975; Vol. 2, Part 11, p 542.

Warowny, W.; Eubank, P. T. Generalized Equations of the Burnett *P*−*V*−*T* Methods for Adsorbing Gases. *Fluid Phase Equilib.* **1995**, *103* (1), 77−95.

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