

Table II. Boiling Point Data of β -Ethoxypropionitrile

Sl no.	P, mmHg	Boiling point °C		α (deviation) ^a in %
		Exptl	Calcd	
1	25	75.1	77.5	+3.2
2	30	81.0	81.4	+0.49
3	40	88.2	87.7	-0.57
4	50	93.5	92.9	-0.64
5	60	97.4	97.2	-0.21
6	70	102.5	100.9	-1.56
7	80	103.7	104.2	+0.48
8	90	106.5	107.2	+0.66
9	100	109.4	109.9	+0.46
10	200	128.6	128.9	+0.23
11	300	141.1	141.0	-0.07
12	400	150.7	150.1	-0.40
13	500	158.5	157.4	-0.69
14	600	164.6	163.7	-0.55
15	760	171.7	172.1	+0.23

^a (Calculated - experimental)/experimental \times 100. Average deviation = 0.696%.

Results

The experimental results are fitted to the Calingaert-Davis equation using the method of least squares. The constants A and B of the Calingaert-Davis equation are found to be 7.6998 and 1937.5, respectively. The equation is as follows:

$$\log P = 7.6998 - (1937.5/(230 + t))$$

where P = pressure in mmHg and t = boiling point, °C.

The calculated values from the above equation are compared with the experimental values (Table II), and the average deviation is found to be 0.696%.

Literature Cited

- (1) Evans, D. P., Davies, W., Jones, W. J., *J. Chem. Soc.*, 1310 (1930).
- (2) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor Liquid Equilibrium", 2d English ed, Translated by G. Standart, Pergamon Press, London, 1967, pp 240, 254.

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Experimental Pressure-Volume-Temperature Relations for Saturated and Compressed Fluid Ethane

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In this paper we present the results of high precision experimental PVT measurements in compressed fluid ethane. The PVT measurements were performed on 22 nearly isochoric samples of ethane whose nominal densities ranged from 0.03 to 0.57 g cm⁻³. In addition to these isochoric measurements, saturated vapor pressures have been measured at temperatures ranging from 214 to 305 K. Saturated liquid densities, thought to be accurate to within a few tenths of one percent, have been obtained from the intersection of the equation of state used to smooth the experimental isochoric data and the vapor pressure curve. The accuracy of the data is estimated to be within 0.2% except in the very neighborhood of the critical point.

There have been three major experimental investigations of pressure-volume-temperature relationships for compressed fluid ethane. The earliest study was performed by Reamer et al. (7) in 1944 and covered the temperature range of 310-510 K, with pressures ranging from 5 to 70 MPa (1 MPa = 9.869 233 atm = 145.0377 psia = 10 bar). Later, Michels et al. (6) published PVT measurements in the range of 273-423 K and 1.5-22 MPa. More recently, Douslin and Harrison (3) have reported comprehensive high precision measurements in the temperature range of 248-623 K with pressures ranging from 1.2 to 41 MPa. Even though these investigations cover a considerable portion

of the PVT surface for ethane (see Figure 1), the low temperature, high density fluid remains uninvestigated.

In an attempt to correct this situation, the PVT relationship for 22 nearly isochoric samples of fluid ethane has been measured. These measurements range in density from 0.03 to 0.57 g cm⁻³ with temperatures ranging from 157 to 340 K at pressures to 70 MPa. Pressure measurements for the saturated vapor over the temperature range of 214-305 K are also reported and graphically compared to the results of other authors. Finally, saturated liquid densities have been obtained from the intersection of the function used to smooth the experimental PVT data and the vapor pressure curve.

Experimental Section

The experimental apparatus and procedure have been described in detail elsewhere (9, 17). Briefly, however, the stainless steel isochoric chamber was charged with ethane to a predetermined pressure, the mass of the charge being determined by differential weighings. The zero pressure volume of the system had been previously determined as a function of temperature by making a series of Burnett (7) type expansions into a reference chamber of known volume. The actual volume of the system at a given temperature and pressure was then calculated by correcting for the pressure distortion of the isochoric chamber (8). The uncertainty in the system volume obtained in this manner was estimated to be less than 0.025%.

Temperatures were measured on the IPTS-1948 using a platinum resistance thermometer which had been calibrated by the manufacturer. (This calibration was traceable to a calibration by the National Bureau of Standards.) These temperatures were then converted to the IPTS-1969 using the tables found in ref 2. The temperature of the system was controlled to within ± 0.002

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Table I. Smoothed Experimental Results for Ethane Isochores^a

ρ , MPa	T , K	ρ , MPa	T , K	ρ , MPa	T , K	ρ , MPa	T , K	ρ , MPa	T , K	ρ , MPa	T , K
0.033 26 g cm ⁻³		0.078 08 g cm ⁻³		0.138 15 g cm ⁻³		0.464 69 g cm ⁻³		0.482 14 g cm ⁻³		0.493 83 g cm ⁻³	
1.7978	263.847	3.5415	290.936	4.7939	305.270	1.8010	241.891	2.7776	232.572	1.0901	223.264
1.8451	267.267	3.6047	292.700	4.8835	306.575	2.6740	243.148	4.0369	234.160	1.3582	223.573
1.8874	270.457	3.6843	294.967	4.9125	306.998	5.0696	246.601	4.9043	235.255	2.6073	225.014
1.9214	273.094	3.7644	297.293	5.0047	302.355	8.7598	251.930	10.8536	242.791	7.1657	230.291
1.9696	276.946	3.8358	299.402	5.0804	309.475	12.3903	257.186	15.8132	249.107	13.2663	237.396
2.0232	281.362	3.8798	300.717	5.1308	310.226	15.5318	261.745	20.3318	254.888	26.3433	252.785
2.1116	288.868	4.0586	308.169	5.2134	311.461	19.3096	267.242	25.9910	262.164	32.2851	259.848
2.2265	298.954	4.2298	311.528	5.4166	314.528	23.8253	273.834	33.0034	271.236	38.7653	267.602
2.3077	306.232	4.4205	317.621	5.5757	316.957	29.9399	282.799	39.1821	279.282	45.4430	275.649
2.4147	315.928	4.6549	325.244	6.1712	326.208	34.8434	290.022	45.0272	286.940	51.0623	282.466
2.5267	326.185	4.8949	333.158	6.4062	329.914	40.3828	298.219	50.7959	294.543	59.8280	293.185
2.5970	332.655	5.2034	343.446	6.6440	333.690	48.0013	309.559	55.6868	301.025		
2.7155	343.612										
0.161 16 g cm ⁻³		0.243 63 g cm ⁻³		0.264 93 g cm ⁻³		0.503 75 g cm ⁻³		0.514 95 g cm ⁻³		0.527 07 g cm ⁻³	
4.8427	305.232	4.8967	305.633	4.8611	305.015	1.7200	216.369	0.8106	208.453	1.6633	199.230
4.9191	306.165	4.9824	306.319	5.0341	306.220	2.1551	216.832	1.4217	209.053	3.5886	200.946
5.0152	307.343	5.0719	307.031	5.2613	307.783	2.3673	217.058	5.8378	213.403	7.8460	204.756
5.0992	308.378	5.2102	308.123	5.4861	309.310	5.8821	220.809	11.0472	218.566	14.6987	210.931
5.2908	310.753	5.6988	311.913	5.7139	310.839	11.4663	226.802	19.5213	227.034	25.7551	220.998
5.6712	315.523	6.3710	316.998	6.2960	314.681	18.9705	234.917	26.1347	233.700	32.8649	227.537
6.0344	320.133	7.1014	322.404	7.0957	319.840	26.4243	243.045	34.0761	241.770	40.9851	235.067
6.3979	324.789	7.8292	327.708	7.0957	319.840	33.5570	250.885	43.6064	251.549	49.2061	242.758
6.7653	329.529	8.6261	333.451	8.0050	325.591	42.1201	260.378	52.6803	260.957	55.8998	249.071
7.1694	334.774	9.4042	339.014	8.9211	331.302	50.6532	269.927	59.8750	268.486	63.5978	256.389
7.7675	342.584	9.9776	343.093	9.8947	337.309	57.9192	278.130	71.2268	280.494	71.1220	263.603
				10.7779	342.720	63.7344	284.744				
						71.4671	293.608				
0.291 34 g cm ⁻³		0.342 08 g cm ⁻³		0.390 56 g cm ⁻³		0.539 49 g cm ⁻³		0.554 64 g cm ⁻³		0.566 02 g cm ⁻³	
4.7917	303.430	3.9075	293.336	2.8861	277.925	1.1806	189.331	1.2419	177.382	0.9996	168.032
4.8478	303.752	3.9954	293.674	2.9677	278.136	1.6928	189.746	2.6915	178.429	1.6767	168.479
4.8844	303.962	4.1072	294.103	3.2161	278.777	5.1936	192.590	4.4351	179.691	3.1254	169.437
4.9499	304.336	4.3113	294.883	3.4528	279.387	12.6145	198.660	8.7045	182.793	5.5836	171.067
5.2256	305.899	4.4512	295.416	3.6529	279.902	20.9115	205.509	16.1795	188.263	9.5053	173.679
5.6805	308.437	4.5502	295.792	4.5946	282.317	30.1597	213.217	25.4988	195.148	15.4628	177.673
6.5318	313.081	4.6140	296.034	5.4667	284.543	39.0914	220.733	34.6140	201.949	23.5404	183.136
7.4635	318.048	5.3018	298.624	6.3258	286.727	48.2857	228.543	43.5599	208.686	31.8991	188.844
8.3937	322.924	6.2081	301.993	7.8630	290.618	60.4011	238.949	52.4640	215.452	41.4739	195.448
9.3726	327.991	7.0249	304.995	10.4743	297.190			61.0168	222.008	49.8074	201.251
10.6260	334.413	8.3069	309.657	13.4666	304.683			67.5191	227.030	57.6863	206.784
12.2475	342.647	9.6434	314.468	16.6485	312.625			70.2139	229.121	65.7032	212.460
		10.9858	319.264	19.9423	320.832					72.5394	217.337
		12.5071	324.667	23.5257	329.753						
		13.6156	328.588	27.6381	339.989						
		15.4913	335.200								
		17.2370	341.335								
0.412 41 g cm ⁻³		0.437 63 g cm ⁻³		0.452 51 g cm ⁻³		0.578 13 g cm ⁻³					
2.6071	269.313	2.2940	257.326	1.9908	249.192	0.5209	157.201				
2.8600	269.861	2.6232	257.911	2.6578	250.248	2.6931	158.496				
3.1732	270.539	3.2730	259.065	4.6318	253.374	4.4999	159.577				
3.5523	271.359	5.7440	263.450	7.9639	258.654	6.5142	160.786				
4.2140	272.788	8.6662	268.631	12.5036	265.858	11.2688	163.656				
6.4519	277.605	11.4107	273.496	16.9763	272.972	16.9322	167.103				
8.4030	281.789	16.8341	283.116	20.7790	279.035	25.3326	172.270				
10.5196	286.317	21.4327	291.287	24.6290	285.189	33.4498	177.321				
12.3976	290.328	25.4120	298.372	30.6459	294.840	42.7266	183.160				
15.1557	296.212	30.3884	307.254	36.6230	304.470	51.3556	188.652				
17.9385	302.145	37.2415	319.529	44.2010	316.744	60.5282	194.552				
21.9583	310.715					67.5565	199.115				
25.8855	319.093					72.6080	202.417				
32.9676	334.225										

^a 1 MPa = 9.869 233 atm = 145.0377 psia = 10 bar.

K by means of a commercial temperature controller. The absolute accuracy of the temperature measurement is believed to be within ± 0.015 K. Pressures were measured by referencing the system pressure to oil pressures derived from an oil dead weight gauge. The estimated accuracy of the pressure measurement was on the order of 0.01% at the highest pressures, increasing to 0.05% at the lowest pressures investigated.

The experimental procedure consisted of charging the ethane to the system and determining the differential mass. After the system reached temperature equilibrium, the temperature and pressure of the sample were recorded. The temperature of the system was then changed and a second pressure was recorded. In this manner, a series of pressure-temperature determinations was made on a constant mass sample. Usually, the temperature

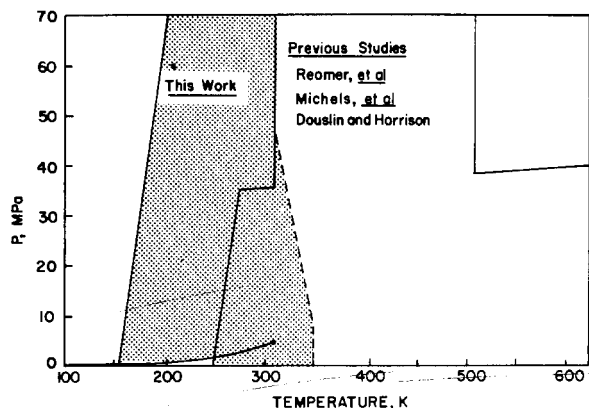


Figure 1. Schematic representation of the P-T surface of ethane and the region of the surface covered by this and previous investigations. Note that this work (the shaded region) constitutes the first investigation of the low temperature, high density fluid.

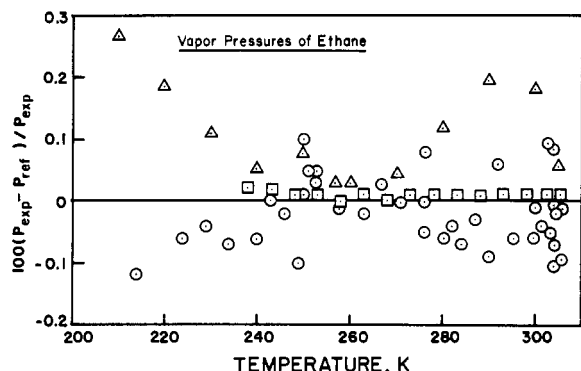


Figure 2. This figure presents a percentage deviation plot of the experimental ethane vapor pressures. The reference values, P_{ref} , were calculated using a correlation proposed by Goodwin (5). Symbol key: \square (3), Δ (4), and \circ this work.

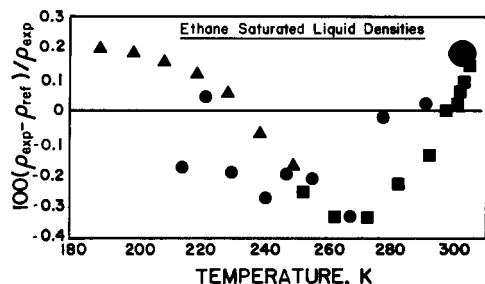


Figure 3. Percentage deviation plot of experimental saturated liquid densities. The reference values were calculated using a correlation proposed by Goodwin (5). Note the qualitative agreement in the systematic trends of the data sets. Symbol key: \blacksquare (3), \blacktriangle (4), and \bullet this work.

of the system was initially set at the highest temperature of interest and then lowered to generate the pseudo-isochoric data. This procedure was adopted so that when the two-phase boundary was reached, measurements could be continued along the vapor pressure curve. For further information as to the experimental apparatus and technique, the reader is referred to ref 11.

The ethane used in this investigation was Phillips Research Grade whose purity was shown to be 99.95% (w/w) by GLC analysis.

Results and Discussion

Due to the temperature and pressure changes in the volume of the isochoric cell, the density of the constant mass sample

Table II. Vapor Pressures of Ethane

T, K	ρ, MPa	T, K	ρ, MPa
214.302	0.3973	282.247	2.9540
221.101	0.5153	284.635	3.1174
224.102	0.5712	287.653	3.3365
229.756	0.6948	288.263	3.3833
234.558	0.8140	290.040	3.5147
239.844	0.9622	292.236	3.6927
240.514	0.9824	293.098	3.7573
243.359	1.0716	296.347	4.0287
246.814	1.1869	299.665	4.3220
247.816	1.2210	300.205	4.3737
249.741	1.2931	300.443	4.3881
250.146	1.3070	301.251	4.4693
251.587	1.3621	303.471	4.6815
252.544	1.3989	303.477	4.6893
254.290	1.4682	304.049	4.7390
257.543	1.6035	304.360	4.7717
263.380	1.8699	304.446	4.7846
267.536	2.0792	304.519	4.7828
271.749	2.3068	304.734	4.8059
275.922	2.5492	304.796	4.8148
276.363	2.5793	304.924	4.8316
276.385	2.5786	304.980	4.8345
276.514	2.5886	305.121	4.8484
277.813	2.6667	305.135	4.8459
280.041	2.8071	305.153	4.8515

Table III. Saturated Liquid Densities of Ethane

T, K	$\rho, g\ cm^{-3}$	T, K	$\rho, g\ cm^{-3}$
215.775	0.503 75	256.493	0.437 63
223.500	0.493 83	268.412	0.412 41
230.486	0.482 14	277.858	0.390 56
241.202	0.464 69	292.736	0.342 08
248.479	0.452 51	301.727	0.291 34
		304.038	0.264 93

was not constant. Thus, after correcting the raw experimental data for volume changes, one actually has measured pseudo rather than true isochoric data. In order to obtain results along a true isochore, the pseudo-isochoric data were fit to an equation of state of the form proposed by Vennix and Kobayashi (10) with appropriate modifications for the temperature and density range covered in this investigation. To minimize the possibility of serious systematic errors in the equation of state, the highly precise data of Douslin and Harrison (3) were included (with equal weight) in the regression analysis. The resulting equation was then used to calculate a Δp for a $\Delta \rho$ where

$$\Delta p = \rho(\text{true isochore}) - \rho(\text{pseudo-isochore})$$

at the experimental temperature. Table I lists the isochoric experimental data that have been obtained in this manner. It should be pointed out that the constant densities listed in Table I differ by only a few tenths of one percent from the experimentally observed densities. In other words the amount of correction being done by the equation of state is very small and should be regarded as a correction for the temperature and pressure distortion of the system. The original unsmoothed experimental data are available upon request. (In addition to the 22 isochores listed in Table I, two additional isochores have been studied, and data are available. These isochores were not included in Table I due to the fact that they are very close to the critical isochore and did not smooth well.)

Table II lists the vapor pressure measurements and Figure 2 compares these measurements to those of Douslin and Harrison

(3) and those reported by Eubank (4). The reference values in Figure 2 are those calculated by Goodwin (5) and have been chosen only as a convenient reference point without regard to their overall accuracy.

Table III lists selected saturated liquid densities which were obtained by calculating the intersection of the smoothed isochores and the vapor pressure curve. Data were not obtained above 304 K due to the difficulties encountered with the smoothing equation in the critical region. Figure 3 graphically compares these densities to those of ref 3 and 4.

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Literature Cited

- (1) Burnett, E. S., *J. Appl. Mech.*, **58A**, 136 (1936).
- (2) *Com. Int. Poids Mes., Metrologia*, **5**, 35 (1969).
- (3) Douslin, D. R., Harrison, R. H., *J. Chem. Thermodyn.* **5**, 491 (1973).
- (4) Eubank, P. T., *Adv. Cryog. Eng.*, **17**, 270 (1971).
- (5) Goodwin, R. D., *Natl. Bur. Stand. Internal Rep.*, NBSIR No. 74-398.
- (6) Michels, A., van Straaten, W., Dawson, J., *Physica (Utrecht)*, **20**, 19 (1954).
- (7) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **36**, 956 (1944).
- (8) Roarck, R. J., "Formulas for Stress and Strain", McGraw-Hill, New York, N.Y., 1954.
- (9) Vennix, A. J., Ph.D. Thesis, Rice University, Houston, Texas, 1966.
- (10) Vennix, A. J., Kobayashi, R., *AIChE. J.*, **15**, 926 (1969).
- (11) Vennix, A. J., Leland, T. W., Kobayashi, R., *Adv. Cryog. Eng.* **12**, 700 (1966).

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Vapor Pressures and Enthalpies of Vaporization of Benzyl Halides

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Vapor pressures over a range of temperatures have been measured for the benzyl halides using an isoteniscope. The calculated enthalpies of vaporization at 25 °C are 44.5 ± 0.4, 50.1 ± 0.5, 50.5 ± 0.5, and 50.6 ± 1.4 kJ mol⁻¹, respectively, for the fluoride, chloride, bromide, and iodide. The enthalpies of fusion of benzyl bromide and iodide, measured by differential scanning calorimetry, are 13.7 ± 0.2 kJ mol⁻¹ at -1.4 °C and 13.2 ± 0.4 kJ mol⁻¹ at 26.3 °C, respectively.

During thermochemical measurements on benzyl halides (2) a literature search revealed that values of the enthalpies of vaporization were available only for the chloride and bromide members of the series, and that these were based on old work (7). Accordingly, a study of the temperature dependence of vapor pressures of all four benzyl halides was undertaken.

Experimental Section

Materials. Benzyl chloride, benzyl bromide, and *n*-heptane (all from British Drug Houses) and benzyl fluoride (P.C.R. Chemicals, Gainesville, Fla.) were dried and fractionally distilled before use. Benzyl iodide was prepared by the method of Coleman and Hauser (5) and purified by fractional crystallization. The purities of these materials, as determined by GLC, are reported in Table I which also includes melting temperatures and enthalpies of fusion. Analyses were by a Philips PV4000 gas-liquid chromatograph, equipped with a 3 m × 2 mm column (10 mass % squalane on diatomite 'C') and a flame ionization detector. Nitrogen was used as a carrier gas. It is considered that this equipment could detect impurities with the exception of water, down to 0.01 mass % or better. Enthalpies of fusion were found by differential scanning calorimetry (Perkin-Elmer DSC-1) only for the bromide and iodide.

Vapor Pressures. Vapor pressures were measured directly by means of an isoteniscope and a vacuum system using standard techniques (11). A closed-ended mercury manometer was

used to record the pressure, the mercury height being read with a cathetometer. Pressures were corrected to 0 °C and standard gravity. The isoteniscope was immersed in a stirred, thermostated oil bath of which the temperature close to the bulb was read by a series of short-range mercury thermometers (British Standards 593) calibrated on the IPTS 68 scale.

Results

Between three and six readings of vapor pressure were taken at each temperature, the mean values of each group being reported in Table II. The scatter of the values about these means was about 0.1 °C and 0.1 mmHg, respectively, although the thermometers could be read to the nearest 0.02 °C and the cathetometer to the nearest 0.01 mm.

The original, unaveraged results were fitted to the Antoine equations

$$\log p \text{ (mmHg)} = A - B/(t + C)$$

by a least-squares procedure with *t* as the independent variable, the value of the constant *C* being first calculated from the correlation given by Kreglewski and Zwolinski (8)

$$C = 273.2 - 0.04T_b - 3 \times 10^{-4}T_b^2$$

where *T_b* (K) is the boiling temperature (Table III). The calculated Antoine constants are presented in Table III together with their

Table I. Purities (GLC), Melting Temperatures, and Enthalpies of Fusion of Benzyl Halides

Compound	Purity, mass %	Melting temp, °C	Δ _f H at melting temp, kJ mol ⁻¹
Benzyl fluoride	99.50		
Benzyl chloride	99.85		
Benzyl bromide	99.80	-1.4	13.7 ± 0.2
Benzyl iodide	99.87	26.3	13.2 ± 0.4