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PVT and Vapor Pressure Measurements on Ethane*

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New measurements of the vapor pressures and *PVT* properties of ethane are reported. *PVT* determinations have been made from near the triple point to 320 K at pressures to 33 MPa. The density range investigated extends to more than three times the critical density. The new measurements of the vapor pressures of ethane extend from 160 K to near the critical point.

Key words: Density; ethane; vapor pressure; *PVT*.

1. Introduction

Liquefied fuel gases, such as LNG, are expected to play an increasing role in satisfying future energy requirements. Accurate thermophysical properties data for these liquefied gas mixtures are necessary for the design of liquefaction plants, transport equipment, shipping and receiving terminals, and for custody transfer. The near infinite variations in mixture compositions encountered with these fuel gases rule out completely experimental or strictly computational approaches for determining these properties. Calculation methods, based on accurate, wide range pure component data and selected mixtures data are being developed in a number of laboratories, and appear to offer the only reliable and economical approach for the generation of the necessary thermophysical properties.

This paper reports new measurements of vapor pressures and *PVT* properties of pure ethane. The measurements have been made as part of a comprehensive program to provide the required experimental data and to develop suitable calculation techniques for mixture properties determinations. *PVT* measurements have been made from near the triple point (90.348 K) [1][1] to 320 K at pressures up to 33 MPa. The density range extends to more than three times the critical density. The new measurements of the vapor pressures extend from 160 K to near the critical temperature (305 K).

2. Experimental Detail

To measure single-phase densities, the gas expansion technique was used. A series of pressure-temperature observations are made on a nearly constant density sample of fluid confined in a cell of accurately calibrated volume. When either the maximum pressure or maximum temperature is reached, the fluid is expanded, to low pressure, into large calibrated volumes maintained at an accurately known temperature above room temperature. The density can then be determined from the cell volume and the compressibility factor (PV/RT) of the ethane at the conditions of the expansion volumes.

The ethane used was commercially available research grade with specified minimum purity of 99.98 percent. This purity was verified by chromatographic analysis. Temperatures were measured on the IPTS (1968) with a platinum resistance thermometer calibrated by the National Bureau of Standards. Pressures above about 3 MPa were measured by referencing to oil pressures derived from an oil dead weight gauge accurate to within 0.015 percent. Lower pressures were measured with a precision fused quartz bourdon tube gauge which had been previously calibrated against an air dead weight gauge accurate to within 0.01 percent. The apparatus and procedures were similar to those used previously in this laboratory for measurements on several other cryogenic fluids [2–5] and have been described in detail [6–8]. Slight modification to existing apparatus was necessary because of the higher critical temperature of ethane. Those external parts of the system which contained fluid during a measurement were heated to well above the critical temperature (typically 330 K) in order to reduce the relative density of the fluid residing in these parts, permitting a more accurate adjusted density to be computed.

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[1] Figures in brackets indicate the literature references at the end of this paper.

3. Results

With the techniques used here, each experimental *PVT* "run" consists of a number of pressure-temperature observations lying along a near-isochoric path. About 50 such runs were made covering a density range of from about 1.5 to over 21.5 mol/l. Each run consisted of from 5 to 16 *PVT* points, depending on the density. Measurements were always made at fixed temperatures to permit direct analysis in terms of isotherms. A total of over 450 *PVT* data points was determined. These data are tabulated along isotherms in table 1.

TABLE 1. PVT *data for ethane*

P (MPa)	ρ (mol/l)
$T=92.00$ K	
0.7928	21.629
$T=93.00$ K	
8.7870	21.682
$T=94.00$ K	
3.5870	21.599
10.4980	21.664
$T=96.00$ K	
6.3091	21.555
14.6217	21.641
$T=98.00$ K	
8.1853	21.503
19.1732	21.625
$T=100.00$ K	
1.7991	21.348
11.3755	21.468
23.8694	21.613
$T=102.00$ K	
4.7964	21.315
15.4890	21.448
28.5382	21.603
$T=104.00$ K	
1.1828	21.198
6.9584	21.269
19.9098	21.434
33.1959	21.594
$T=106.00$ K	
9.0567	21.221
24.4329	21.422
$T=108.00$ K	
1.8227	21.065
6.4514	21.125
12.4806	21.193
29.0045	21.412
$T=110.00$ K	
4.7101	21.034
16.4766	21.176
33.5810	21.403
$T=112.00$ K	
1.1911	20.911
6.8417	20.990
11.2851	21.041
20.6898	21.163
$T=114.00$ K	
3.8739	20.882
8.8149	20.942
24.9715	21.152
$T=116.00$ K	
1.9636	20.776
6.3156	20.841
12.0035	20.913
19.0660	21.009
29.2820	21.143
$T=118.00$ K	
8.0478	20.791
15.7492	20.896
23.2017	20.997
$T=120.00$ K	
1.2747	20.621
6.8130	20.702
10.8020	20.757
19.6919	20.883
27.3594	20.988
$T=122.00$ K	
3.8664	20.592
14.2998	20.737
23.7193	20.873
31.5310	20.979
$T=124.00$ K	
6.2436	20.553
11.6827	20.627
18.0492	20.724
27.7606	20.863
$T=126.00$ K	
7.9236	20.505
21.9553	20.712
31.8410	20.855
$T=128.00$ K	
0.6715	20.312
10.4787	20.470
18.8911	20.597
25.8617	20.703
35.9026	20.847
$T=130.00$ K	
2.9285	20.287
13.7499	20.450
29.7809	20.694
$T=132.00$K	
5.4980	20.254
17.2765	20.436
26.4639	20.577
33.6963	20.687
$T=134.00$ K	
7.2368	20.209
20.8906	20.425
$T=136.00$ K	
1.3689	20.030
9.2490	20.167
24.5518	20.416
34.0682	20.561
$T=138.00$ K	
3.7831	20.008
12.1243	20.144
28.2309	20.407
$T=140.00$ K	
6.0574	19.972
15.3375	20.129
31.9091	20.400
$T=142.00$ K	
7.6559	19.926
18.7024	20.117
35.5822	20.392
$T=144.00$ K	
0.9387	19.722
9.8460	19.890
22.1094	20.107
$T=148.00$ K	
5.4489	19.667
15.7717	19.856
28.9678	20.091
$T=152.00$ K	
1.2079	19.424
8.9240	19.584
22.1746	19.836
35.8308	20.077
$T=156.00$ K	
5.5978	19.369
14.2846	19.545
28.6589	19.820
$T=160.00$ K	
0.4675	19.091
8.9636	19.288
20.2324	19.524
35.1468	19.806
$T=164.00$ K	
4.2580	19.043
14.0474	19.250
26.2885	19.508
$T=168.00$ K	
1.7297	18.817
7.6437	18.969
19.6507	19.230
32.3436	19.495
$T=172.00$ K	
1.2449	18.650
5.7607	18.768
11.8776	18.916
25.3400	19.214
38.3722	19.482
$T=176.00$ K	
1.1073	18.488
5.2091	18.602
8.8759	18.691
16.9907	18.892
31.0365	19.201
$T=180.00$ K	
0.5247	18.295
4.9583	18.442
8.2782	18.525
13.3001	18.655
22.2633	18.876
36.7092	19.189
$T=184.00$ K	
3.9725	18.253
7.9795	18.368
12.4806	18.483
18.2646	18.635
27.5482	18.862

TABLE 1. PVT *data for ethane*—Continued

P (MPa)	ρ (mol/l)
$T = 188.00$ K	
1.9817	18.021
7.2058	18.186
11.9718	18.323
17.2059	18.463
23.3273	18.620
32.8340	18.850
$T = 192.00$ K	
0.9865	17.815
5.5964	17.977
10.6669	18.128
16.5186	18.302
22.0330	18.447
28.3464	18.607
$T = 196.00$ K	
0.4943	17.619
4.4533	17.775
8.4330	17.903
14.9662	18.104
21.1586	18.286
26.8669	18.434
33.3677	18.595
$T = 200.00$ K	
0.6801	17.445
3.5738	17.581
7.3933	17.709
12.2367	17.866
19.4175	18.087
25.8517	18.273
31.6945	18.423
$T = 204.00$ K	
3.7760	17.411
6.7420	17.524
10.6983	17.658
16.4076	17.846
23.9051	18.074
30.2305	18.262
36.4896	18.412
$T = 208.00$ K	
0.5897	17.079
6.8033	17.354
9.6616	17.461
14.6253	17.634
20.6552	17.831
28.3791	18.062
35.0871	18.251
$T = 212.00$ K	
3.4269	17.048
9.6570	17.293
13.3583	17.434
18.6673	17.619
24.9088	17.819
32.8419	18.051

P (MPa)	ρ (mol/l)
$T = 216.00$ K	
2.1043	16.798
6.4050	16.998
13.2349	17.267
17.2225	17.417
22.7370	17.606
29.1542	17.808
$T = 220.00$ K	
1.4301	16.567
5.1249	16.761
8.9985	16.934
16.9669	17.250
21.1113	17.404
26.8053	17.594
33.3471	17.798
$T = 224.00$ K	
4.3322	16.536
7.6124	16.699
12.2714	16.904
20.7255	17.237
25.0127	17.392
30.8565	17.584
$T = 228.00$ K	
1.8552	16.198
6.9228	16.483
10.4762	16.654
15.7164	16.887
24.4895	17.225
28.8946	17.382
34.8859	17.574
$T = 232.00$ K	
1.2667	15.950
4.5825	16.167
9.4583	16.428
13.6904	16.633
19.2025	16.874
28.2402	17.215
32.7523	17.372
$T = 236.00$ K	
3.8508	15.920
7.0049	16.114
12.4747	16.403
16.9765	16.618
22.6904	16.862
31.9811	17.205
$T = 240.00$ K	
1.2548	15.515
2.2021	15.586
6.3368	15.877
9.4209	16.062
15.5972	16.387
20.2787	16.606
26.1772	16.852
35.7046	17.196

P (MPa)	ρ (mol/l)
$T = 244.00$ K	
3.6366	15.487
4.6703	15.556
8.5355	15.817
12.2246	16.039
18.7424	16.375
23.5869	16.595
29.6476	16.842
$T = 248.00$ K	
1.7380	15.078
5.9925	15.449
6.8908	15.508
11.1353	15.788
15.1129	16.023
21.8905	16.364
26.8798	16.586
33.1044	16.833
$T = 252.00$ K	
1.5930	14.811
3.9746	15.056
8.0325	15.392
9.0553	15.457
13.8649	15.771
18.0296	16.011
25.0394	16.354
30.1617	16.577
$T = 256.00$ K	
3.7062	14.790
6.1397	15.018
10.3740	15.358
11.5324	15.433
16.6249	15.758
20.9491	16.000
28.1716	16.345
33.4255	16.568
$T = 260.00$ K	
2.6858	14.414
5.7990	14.757
8.0637	14.963
12.8526	15.340
14.0783	15.417
19.3947	15.747
23.8662	15.990
31.2936	16.336
$T = 264.00$ K	
2.4038	14.085
4.6766	14.389
7.6561	14.705
10.2294	14.931
15.3689	15.327
16.6466	15.405
22.1619	15.737
26.7721	15.981
34.3986	16.328

P (MPa)	ρ (mol/l)
$T = 268.00$ K	
3.0548	13.884
4.2654	14.062
6.5471	14.352
9.6680	14.669
12.5033	14.914
17.8943	15.316
19.2306	15.395
24.9268	15.728
29.6684	15.973
$T = 272.00$ K	
2.0844	1.243
3.6257	13.670
4.8506	13.859
6.0679	14.032
8.2942	14.302
11.8077	14.650
14.8065	14.901
20.4232	15.306
21.8042	15.385
27.6780	15.719
32.5542	15.964
$T = 276.00$ K	
2.1376	1.242
3.2684	13.256
5.3267	13.644
6.5457	13.824
7.7197	13.983
10.2212	14.275
13.9836	14.636
17.1196	14.890
22.9462	15.297
24.3837	15.377
30.4166	15.711
35.4306	15.957
$T = 280.00$ K	
2.1904	1.241
2.9758	12.787
4.8428	13.234
6.9195	13.604
8.1526	13.778
9.4890	13.951
12.2137	14.259
16.1653	14.625
19.4376	14.880
25.4635	15.288
26.9473	15.368
33.1520	15.703
$T = 284.00$ K	
2.2428	1.240
4.3982	12.768
6.3596	13.203
8.4885	13.563
9.8840	13.751
11.3395	13.933
14.2261	14.247
18.3557	14.615
21.7505	14.872
27.9731	15.280
29.4971	15.360
35.8724	15.696

TABLE 1. PVT *data for ethane*—Continued

P (MPa)	ρ (mol/l)
$T=288.00$ K	
2.2951	1.239
3.0547	1.955
3.9706	12.194
5.8026	12.745
7.7971	13.160
10.1657	13.540
11.6682	13.735
13.2063	13.920
16.2439	14.237
20.5477	14.607
24.0580	14.863
30.4719	15.273
32.0446	15.353
$T=292.00$ K	
2.3466	1.239
3.8113	11.522
5.2158	12.173
7.1396	12.707
9.3105	13.131
11.8771	13.525
13.4688	13.723
15.0863	13.910
18.2640	14.228
22.7394	14.598
26.3645	14.855
32.9673	15.265
$T=296.00$ K	
2.3987	1.238
3.2373	1.952
3.8806	2.880
4.3963	11.212
4.8686	11.505
6.4389	12.146
8.4817	12.672
10.8697	13.115
13.6040	13.514
15.2773	13.713
16.9735	13.900
20.2846	14.219
24.8761	14.591
28.6475	14.848
35.4484	15.258
$T=300.00$ K	
2.4492	1.237
4.0309	2.875
4.6932	10.611
5.3970	11.196
5.9485	11.485
7.6275	12.109
9.8845	12.652
12.4490	13.102
12.4489	13.102
15.3377	13.504
17.0906	13.704
18.8621	13.892
22.3018	14.211
27.0931	14.583
30.9501	14.841
$T=304.00$ K	
2.4997	1.237
3.4158	1.950
4.1784	2.873
4.6828	4.325
4.7721	9.097
4.9674	9.788
5.3930	10.298
5.5668	10.596
6.3948	11.173
6.9986	11.455
8.8474	12.082
11.3086	12.638
14.0362	13.092
17.0942	13.495
18.9013	13.696
20.7454	13.884
24.3137	14.204
29.2629	14.576
33.2309	14.833
$T=306.00$ K	
4.8094	4.323
4.9441	6.533
5.0757	9.092
5.8014	10.290
$T=308.00$ K	
2.5499	1.236
4.3236	2.871
4.9341	4.321
5.1434	6.530
5.3872	9.086
5.6969	9.775
6.2111	10.280
6.4452	10.574
7.3779	11.142
8.0352	11.424
10.0940	12.066
12.7418	12.628
15.6258	13.083
18.6310	13.487
20.7132	13.688
22.6296	13.876
26.3246	14.196
31.4261	14.569
35.5024	14.826
$T=312.00$ K	
2.5996	1.235
3.5908	1.947
4.4668	2.869
5.1793	4.316
5.5401	6.522
6.0206	9.072
6.4330	9.756
7.0307	10.254
7.3179	10.546
8.3744	11.116
9.1114	11.404
11.3574	12.054
14.1819	12.618
17.2177	13.075
20.5666	13.480
22.5240	13.681
24.5119	13.869
28.3286	14.189
33.5824	14.562
$T=316.00$ K	
2.6491	1.235
4.6083	2.866
5.4200	4.312
5.9358	6.513
6.6610	9.054
7.1729	9.732
7.8532	10.229
8.1986	10.522
9.3878	11.099
10.1982	11.390
12.6240	12.044
18.8045	13.068
22.3004	13.472
24.3313	13.673
26.3890	13.862
30.3236	14.183
$T=320.00$ K	
2.6983	1.234
3.7629	1.945
4.7483	2.864
5.6574	4.307
6.3309	6.503
7.3064	9.032
7.9172	9.710
8.6869	10.211
9.0937	10.506
10.4137	11.087
11.2486	11.380
13.9007	12.036
17.0663	12.602
20.4014	13.060
24.0318	13.466
26.1304	13.667
28.2588	13.855
32.3174	14.176

Although comparison with data from other sources is, in general, impossible without multiple interpolations, the agreement has been deduced by examining the density deviations of the various data sets [9, 10] from densities calculated from an equation of state for ethane due to Goodwin [11]. The agreement is found to be, in general, within the combined experimental error. Maximum difference occur in the critical region where the equation of state representation is expected to be less satisfactory and where the experimental densities are subject to increasing uncertainty. Estimated uncertainty in the experimental densities in this work is typically ± 0.1 percent at the lowest temperatures, increasing to ± 0.2 percent at higher temperatures and lower densities, becoming as much as ± 1.0 percent in the critical region.

New vapor pressure measurements also have been made at 5 K intervals from 160 to 300 K and are given in table 2. At each temperature, the pressure was measured at least twice with some ethane being removed from the cell between measurements. Identical pressure observations indicated that the two-phase condition existed in the cell.

A vapor pressure equation of the form

$$ln(P/P_t)=A\chi+B\chi^2+C_x{}^3+D\chi^4+E\chi(1-\chi)^{3/2} \quad (1)$$

was fit to all available data for ethane [12]. Here, $\chi=(1-T_t/T)/(1-T_t/T_c)$, and P and T are the pressure and temperature and t and c refer to the triple and critical points. Coefficients giving the best fit were found to be the following:

$A = 10.67324$
$B = 8.33782$
$C = -3.08489$
$D = -0.65857$
$E = 6.04955$
$P_t = 1.14 \times 10^{-5}$ bar
$T_t = 90.348\ K$ [Ref 1]
$T_c = 305.330$ K [Ref 10]

TABLE 2

T (K)	P kPa	T (K)	P kPa
160.00	21.502	230.00	700.48
165.00	30.670	235.00	825.96
170.00	42.870	240.00	966.60
175.00	58.636	245.00	1124.4
180.00	78.734	245.00	1124.8
180.00	78.706	250.00	1300.0
185.00	103.84	250.00	1301.9
190.00	134.63	250.00	1302.1
190.00	134.72	250.00	1301.8
195.00	172.21	255.00	1495.0
195.00	172.26	260.00	1670.3
200.00	217.26	265.00	1947.9
200.00	217.32	270.00	2208.0
205.00	270.93	275.00	2493.1
205.00	271.00	275.00	2493.2
210.00	334.13	280.00	2804.6
210.00	334.17	280.00	2806.2
210.00	333.98	285.00	3144.3
210.00	333.99	290.00	3513.5
215.00	407.34	298.15	4190.9
220.00	492.16	298.15	4188.9
225.00	589.73	300.00	4353.5

Deviations of the experimental vapor pressures from those calculated from this equation for the various data sets [9, 10, 13] are shown in figure 1.

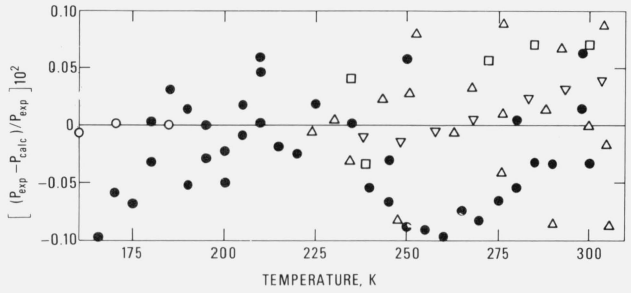

FIGURE 1. *Deviations of vapor pressures from* eq. 1.

● This work; ○ Ziegler et al. (Ref. [13]); △ Pal (Ref. [9]); □ Pope (Ref. [9]); ▽ Douslin and Harrison (Ref. [10]).

4. Summary

We have made new wide-range measurements of the vapor pressures and *PVT* properties of ethane. These are the only data currently available which cover the entire temperature range from the triple point to 320 K. In addition, these data are the only accurate *PVT* data available for the compressed liquid below about 190 K. The data are being used along with other available data to refine the calculation of thermodynamic functions for ethane and as input to, and as a check upon, new calculation methods for predicting liquefied natural (fuel) gas properties being studied in this and other laboratories.

5. References and Notes

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