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] 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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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

| $T$ (K) | $P$ (MPa) | $\rho$ (mol/l) | $T$ (K) | $P$ (MPa) | $\rho$ (mol/l) | $T$ (K) | $P$ (MPa) | $\rho$ (mol/l) | $T$ (K) | $P$ (MPa) | $\rho$ (mol/l) |
|---------|-----------|----------------|---------|-----------|----------------|---------|-----------|----------------|---------|-----------|----------------|
| 92.00   | 0.7928    | 21.629         | 112.00  | 1.1911    | 20.911         | 130.00  | 2.9285    | 20.287         | 156.00  | 5.5978    | 19.369         |
| 93.00   | 8.7870    | 21.682         | 114.00  | 3.8739    | 20.882         | 132.00  | 5.4980    | 20.254         | 160.00  | 0.4675    | 19.091         |
| 94.00   | 3.5870    | 21.599         | 116.00  | 1.9636    | 20.776         | 134.00  | 1.3689    | 20.030         | 168.00  | 1.7297    | 18.817         |
| 96.00   | 6.3091    | 21.555         | 118.00  | 8.0478    | 20.791         | 136.00  | 3.7831    | 20.008         | 172.00  | 1.2449    | 18.650         |
| 98.00   | 8.1853    | 21.503         | 120.00  | 1.2747    | 20.621         | 138.00  | 3.1243    | 20.144         | 176.00  | 3.1073    | 18.488         |
| 100.00  | 1.7991    | 21.348         | 122.00  | 3.8664    | 20.592         | 140.00  | 6.0574    | 19.972         | 180.00  | 5.8267    | 18.620         |
| 102.00  | 11.3755   | 21.468         | 124.00  | 6.2436    | 20.553         | 142.00  | 3.1909    | 20.400         | 184.00  | 0.5247    | 18.295         |
| 104.00  | 23.8694   | 21.613         | 126.00  | 11.6827   | 20.627         | 144.00  | 0.9387    | 19.722         | 188.00  | 4.9583    | 18.442         |
| 106.00  | 1.1828    | 21.198         | 128.00  | 18.0492   | 20.724         | 146.00  | 9.8460    | 19.890         | 192.00  | 8.2782    | 18.525         |
| 108.00  | 6.9584    | 21.269         | 130.00  | 27.7606   | 20.863         | 148.00  | 22.1094   | 20.107         | 196.00  | 13.3001   | 18.655         |
|         | 19.9098   | 21.434         | 132.00  | 7.9236    | 20.505         | 150.00  | 5.4489    | 19.667         | 200.00  | 22.2633   | 18.876         |
|         | 33.1959   | 21.594         | 134.00  | 21.9553   | 20.712         | 152.00  | 15.7717   | 19.856         | 204.00  | 36.7092   | 19.189         |
|         | 28.5382   | 21.603         | 136.00  | 31.8410   | 20.855         | 154.00  | 28.9678   | 20.091         | 208.00  | 31.0365   | 19.201         |
|         | 24.4329   | 21.422         | 138.00  | 29.0045   | 21.412         | 156.00  | 33.5810   | 20.847         | 212.00  | 33.5810   | 19.201         |
| T (K) | P (MPa) | \(\rho\) (mol/I) | T (K) | P (MPa) | \(\rho\) (mol/I) | T (K) | P (MPa) | \(\rho\) (mol/I) | T (K) | P (MPa) | \(\rho\) (mol/I) |
|-------|--------|-----------------|-------|--------|-----------------|-------|--------|-----------------|-------|--------|-----------------|
| 188.00 | 1.9817 | 18.021          | 216.00 | 2.0143 | 16.798          | 244.00 | 3.6366 | 15.487          | 268.00 | 3.0548 | 13.884          |
| 192.00 | 0.9865 | 17.815          | 220.00 | 1.4301 | 16.567          | 248.00 | 1.7380 | 15.078          |       |        |                 |
| 196.00 | 0.4943 | 17.619          | 224.00 | 5.9925 | 15.449          | 272.00 | 2.0844 | 1.243           |       |        |                 |
| 200.00 | 0.6801 | 17.445          | 228.00 | 5.9925 | 15.449          | 276.00 | 3.2684 | 13.256          |       |        |                 |
| 204.00 | 3.7760 | 17.111          | 232.00 | 3.7062 | 14.790          |       |        |                 |       |        |                 |
| 208.00 | 0.5897 | 17.079          | 236.00 | 3.7062 | 14.790          |       |        |                 |       |        |                 |
| 212.00 | 3.4269 | 17.048          | 240.00 | 2.4038 | 14.085          |       |        |                 |       |        |                 |
| 216.00 | 9.6570 | 17.293          | 244.00 | 4.6766 | 14.389          |       |        |                 |       |        |                 |
| 220.00 | 13.3583 | 17.434         | 248.00 | 7.6561 | 14.705          |       |        |                 |       |        |                 |
| 224.00 | 18.6673 | 17.619         | 252.00 | 10.2212 | 14.275        |       |        |                 |       |        |                 |
| 228.00 | 24.9088 | 17.819         | 256.00 | 12.2367 | 17.866        |       |        |                 |       |        |                 |
| 232.00 | 32.8419 | 18.051         | 260.00 | 10.2212 | 14.275        |       |        |                 |       |        |                 |
| 236.00 | 0.5897 | 17.079          | 264.00 | 10.2212 | 14.275        |       |        |                 |       |        |                 |
| 240.00 | 3.4269 | 17.048          | 268.00 | 10.2212 | 14.275        |       |        |                 |       |        |                 |

Table 1. PVT data for ethane—Continued
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

\[ \ln(P/P_o) = A_s + B_x^2 + C_x^3 + D_x^4 + E_x(1 - x)^{3/2} \]  

was fit to all available data for ethane [12]. Here, \( x = (1 - T/T_c)/(1 - T/T_c) \), 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:

Table 1. PVT data for ethane—Continued

| \( P \) (MPa) | \( \rho \) (mol/l) | \( P \) (MPa) | \( \rho \) (mol/l) | \( P \) (MPa) | \( \rho \) (mol/l) |
|-------|-------|-------|-------|-------|-------|
| \( T = 288.00 \) K | \( T = 300.00 \) K | \( T = 308.00 \) K | \( T = 316.00 \) K |
| 2.2951 | 1.239 | 2.4492 | 1.237 | 2.5499 | 1.236 | 2.6491 | 1.235 |
| 3.8547 | 1.955 | 4.0309 | 2.875 | 4.3236 | 2.871 | 4.6083 | 2.866 |
| 3.9706 | 1.2194 | 4.6932 | 10.611 | 4.9341 | 4.321 | 5.4200 | 4.312 |
| 5.8026 | 12.745 | 5.3970 | 11.196 | 5.1434 | 6.530 | 5.9358 | 6.513 |
| 7.7971 | 13.160 | 5.9485 | 11.485 | 5.3872 | 9.086 | 6.6610 | 9.054 |
| 10.1657 | 13.540 | 7.6275 | 12.109 | 5.6969 | 9.775 | 7.7129 | 9.732 |
| 11.6682 | 13.735 | 9.8845 | 12.652 | 6.2111 | 10.280 | 7.8532 | 10.229 |
| 13.2063 | 13.920 | 12.4490 | 14.285 | 6.4452 | 10.574 | 8.1986 | 10.522 |
| 16.2439 | 14.237 | 12.4489 | 14.104 | 7.3779 | 11.142 | 9.3878 | 11.099 |
| 20.3477 | 14.607 | 15.3377 | 16.504 | 8.0852 | 13.424 | 10.1982 | 11.390 |
| 24.0580 | 14.863 | 17.0906 | 13.704 | 10.0940 | 12.066 | 12.6240 | 12.044 |
| 30.4179 | 15.273 | 18.8621 | 13.892 | 12.7418 | 12.628 | 18.8045 | 13.068 |
| 32.0446 | 15.353 | 22.3018 | 14.211 | 15.6258 | 13.083 | 22.3004 | 13.472 |
| 32.9673 | 15.265 | 27.0931 | 14.583 | 18.6310 | 13.487 | 24.3313 | 13.673 |
| 32.0446 | 15.353 | 28.9501 | 14.841 | 20.7132 | 13.688 | 26.3890 | 13.686 |
| \( T = 292.00 \) K | \( T = 304.00 \) K | \( T = 306.00 \) K | \( T = 320.00 \) K |
| 2.3466 | 1.239 | 2.4997 | 1.237 | 2.5996 | 1.235 | 2.6983 | 1.234 |
| 3.8113 | 11.522 | 3.4158 | 1.950 | 3.5908 | 1.947 | 3.7629 | 1.945 |
| 5.2158 | 12.173 | 4.1784 | 2.873 | 4.4668 | 2.869 | 4.7483 | 2.864 |
| 7.1396 | 12.707 | 4.6828 | 3.325 | 5.1793 | 3.416 | 5.6574 | 3.407 |
| 9.3105 | 13.131 | 4.7721 | 3.997 | 5.5401 | 4.622 | 6.3009 | 4.503 |
| 11.8771 | 13.525 | 4.9674 | 3.978 | 6.0206 | 9.072 | 7.0964 | 9.032 |
| 13.4688 | 13.723 | 5.9390 | 10.298 | 6.4330 | 9.756 | 7.9172 | 9.710 |
| 15.0863 | 13.910 | 5.5668 | 10.596 | 7.0307 | 10.254 | 8.8685 | 10.211 |
| 18.2640 | 14.228 | 6.3948 | 11.173 | 7.3179 | 10.546 | 8.6687 | 10.211 |
| 22.7394 | 14.598 | 8.8474 | 12.062 | 8.3744 | 11.116 | 9.0937 | 10.506 |
| 26.3645 | 14.855 | 11.3086 | 12.638 | 9.1114 | 11.404 | 10.4137 | 11.087 |
| 32.9673 | 15.353 | 14.0362 | 13.092 | 11.3574 | 12.054 | 11.2486 | 11.380 |
| 32.9673 | 15.353 | 17.0942 | 13.495 | 14.1819 | 12.618 | 13.9007 | 12.036 |
| 15.2773 | 15.713 | 18.9013 | 13.696 | 17.2177 | 13.075 | 17.0665 | 12.602 |
| 16.9735 | 15.900 | 20.7454 | 13.884 | 20.5666 | 13.480 | 20.4014 | 13.060 |
| 20.2846 | 14.219 | 24.3137 | 14.204 | 22.5240 | 13.681 | 24.0318 | 13.466 |
| 24.8761 | 14.591 | 29.3629 | 14.576 | 24.5119 | 13.869 | 26.3304 | 13.667 |
| 26.6475 | 14.848 | 33.2599 | 14.833 | 28.2286 | 14.189 | 28.2588 | 13.855 |
| 35.4484 | 15.258 | 5.8014 | 10.290 | 33.5824 | 14.826 | 32.3174 | 14.176 |

\( t = 312.00 \) K
\[ A = 10.67324 \]
\[ B = 8.33782 \]
\[ C = 3.08489 \]
\[ D = -0.65857 \]
\[ P_0 = 1.14 \times 10^{-5} \text{ bar} \]
\[ T_0 = 90.348 \text{ K [Ref 1]} \]
\[ T_c = 305.330 \text{ K [Ref 10]} \]

### 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      | 250.00     | 1124.8      |
| 185.00     | 78.706      | 250.00     | 1300.0      |
| 190.00     | 103.84      | 250.00     | 1301.9      |
| 195.00     | 134.63      | 250.00     | 1302.1      |
| 200.00     | 134.72      | 250.00     | 1301.8      |
| 205.00     | 172.21      | 255.00     | 1405.0      |
| 210.00     | 172.26      | 260.00     | 1670.3      |
| 215.00     | 217.26      | 265.00     | 1947.9      |
| 220.00     | 217.32      | 270.00     | 2208.0      |
| 225.00     | 270.93      | 275.00     | 2493.1      |
| 230.00     | 271.00      | 275.00     | 2493.2      |
| 235.00     | 334.13      | 280.00     | 2904.6      |
| 240.00     | 334.17      | 280.00     | 2906.2      |
| 245.00     | 333.98      | 285.00     | 3144.3      |
| 250.00     | 333.99      | 290.00     | 3513.5      |
| 255.00     | 407.34      | 298.15     | 4190.9      |
| 260.00     | 492.16      | 298.15     | 4188.9      |
| 265.00     | 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.](image)

\[ * \] This work; \( \odot \) Ziegler et al. (Ref. [13]); \( \triangle \) Pal (Ref. [9]); \( \square \) Pope (Ref. [9]); \( \diamond \) Dousslin and Harrison (Ref. [10]).

### 4. Summary

We have made new wide-range measurements of the vapor pressures and \( \text{PVT} \) 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 \( \text{PVT} \) 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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[12] Further refinements in the correlation are expected which will probably alter slightly the final values of the constants. The deviation plot, however, is representative of the agreement among data sets. Coefficients for this equation will be included in the final report. See also reference [8].
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