Measurements of Vapor Pressures from 280 to 369 K and (p, ρ, T) Properties from 340 to 400 K at Pressures to 200 MPa for Propane[1]

H. Miyamoto[2,3] and M. Uematsu[4]

Measurements of (p, ρ, T) properties for compressed liquid propane have been obtained by means of a metal-bellows variable volumometer at temperatures from 340 to 400 K at pressures up to 200 MPa. The volume-fraction purity of the propane sample was 0.9999. The expanded uncertainties $(k = 2)$ of temperature, pressure, and density measurements have been estimated to be less than 3 mK; 1.5 kPa $(p \leqq 7\,\text{MPa})$, 0.06% $(7\,\text{MPa} < p \leqq 50\,\text{MPa})$, 0.1% $(50\,\text{MPa} < p \leqq 150\,\text{MPa})$, and 0.2% $(p > 150\,\text{MPa})$; and 0.11%, respectively. Four (p, ρ, T) measurements at the same temperatures and pressures as literature values have been conducted for comparisons. In addition, vapor pressures were measured at temperatures from 280 to 369 K. Furthermore, comparisons of available equations of state with the present measurements are reported.

KEY WORDS: $p\rho T$ measurements; propane; vapor pressure.

1. INTRODUCTION

In previous publications [1,2] we reported measurements of the vapor pressure and (p, ρ, T) properties for isobutane by a metal-bellows variable volumometer at temperatures from 280 to 440 K at pressures up to

---

Table I.   Experimental $p\rho T$ Property Data for Propane

| First author	Data	Method	p (MPa)	$\rho(\text{kg·m}^{-3})$	T (K)
Reamer [3]	306	Mercury piezometer	0.1–69	1–576	311–511
Dittmer [4]	336	Isochoric method	1.0–103	320–590	273–413
Ely [5]	222	Isochoric method	0.3–43	508–652	166–324
Thomas [6]	736	Mercury piezometer	0.6–40	35–549	258–623
Haynes [7]	196	Magnetic suspension densimeter	0.6–37	493–741	90–300
Kratzke [8]	60	Isochoric method	2.2–61	441–565	247–491
Straty [9]	144	Burnett expansion (isochoric)	0.2–35	2–347	363–598
Claus [10]	130	Single-sinker densimeter	2.0–30	24–506	340–520
Glos [11]	72	Two-sinker densimeter	0.2–12	3–727	95–340
Kayukawa [12]	192	Vibrating tube densimeter	0.2–7	12–579	240–380
This work	63	Bellows variable volumometer	3.0–200	335–631	340–400

200 MPa. In this paper, the results of (p, ρ, T) measurements for propane using the same apparatus are presented for the compressed liquid phase for temperatures from 340 to 400 K at pressures up to 200 MPa. In addition, vapor pressure measurements from 280 to 369 K are also reported.

As for propane, several sets of (p, ρ, T) data were reported in the literature as summarized in Table I. Thomas and Harrison [6] measured 736 points of (p, ρ, T) data in the temperature range from 258 to 623 K at pressures up to 40 MPa by means of a mercury piezometer. Prior to 1984, most measurements have been executed by using a volumometer, for direct density determinations, except for the precise measurements by Haynes [7]. On the other hand, comparatively new information for (p, ρ, T) property measurements were reported from 2002 to 2005 as summarized in Table I. These sets of accurate measurements from three sources were obtained by means of buoyancy methods (single-sinker densimeter below 30 MPa [10] and two-sinker densimeter below 12 MPa [11]) and vibrating tube densimeter below 7 MPa [12].

2. EXPERIMENTAL

The measurements of this study were carried out using the same apparatus as employed in previous work [1, 2]. The experimental procedures are described in detail elsewhere [13].

A schematic diagram of the present experimental apparatus is shown in Fig. 1. A sample of known mass was loaded into a bellows container in a pressure vessel. Nitrogen gas from a pressure-measuring system was supplied to the outside of the bellows container to compress, or
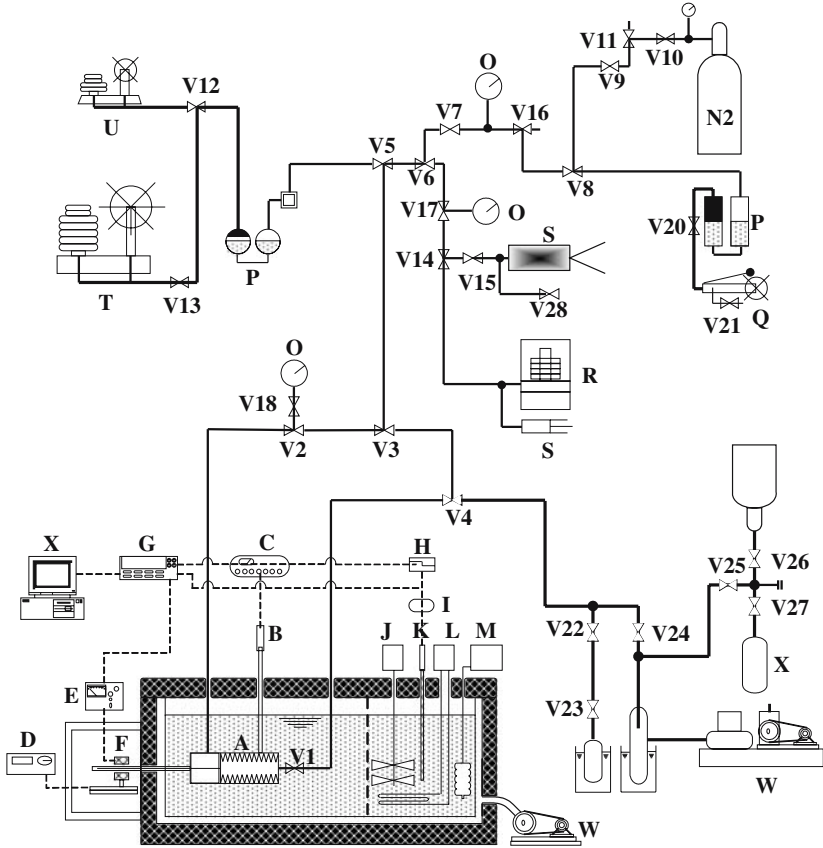
Fig. 1. Schematic diagram of the present apparatus. A: pressure vessel and bellows, B: platinum resistance thermometer, C: thermometer bridge, D: digital indicator, E: galvanometer, F: linear variable differential transformer, G: digital multimeter, H: P.I.D. controller, I: thyristor regulator, J: stirrer, K: sub-heater, L: main heater, M: cooler, O: Bourdon gauge, P: N_2-to-Hg-to-oil separator, Q: hand pump, R: air-piston pressure gauge, S: pressure controller, T: oil-operated dead-weight pressure gauge (30–200 MPa), U: oil-operated dead-weight pressure gauge (7–30 MPa), V: valves, W: vacuum pump, X: personal computer.

expand, the bellows. The pressure of the nitrogen gas was measured with three different pressure gauges depending on the pressure ranges: an air-piston pressure gauge (Ruska: Model 2465) for $p \leqq 7$ MPa, and two oil-operated dead-weight pressure gauges (Futaba: Model T and Model TL2) for 7 MPa $< p < 30$ MPa and $p \geqq 30$ MPa, respectively. The nitrogen gas was pressurized up to 200 MPa with a pressure intensifier using a hand pump and controlled by a screw pump. The pressure of the nitrogen gas was

transmitted to the oil-operated dead-weight pressure gauges with the help of a nitrogen-to-mercury-to-oil separator. The pressure of the sample was obtained by subtracting the difference between the internal and external pressures of the bellows from the pressure values of the nitrogen gas outside the bellows.

The pressure vessel was immersed in a thermostatted oil bath filled with 110L of silicone oil. The temperature was measured with a 25Ω platinum resistance thermometer (Tinsley: 5187SASS), which was inserted into a well drilled in the pressure vessel, using a thermometer bridge (Tinsley: Type 5840DS). The density of the sample could be changed by increasing or decreasing the pressure of the nitrogen gas along each isotherm. The volume change of the bellows was detected by the bellows displacement with a linear variable differential transformer with a resolution of 0.5μm. After the sample had been confirmed to be in thermodynamic equilibrium by monitoring the variation of temperature and the piston of the bellows, we finally obtained (p,ρ,T) values of the sample in the bellows.

3. RESULTS OF CALIBRATION AND ERROR ANALYSIS

In the present study, we chose a coverage factor $k = 2$ and, therefore, the confidence level in the present measurements was estimated to be about 95%. We are considering that no more elements of uncertainty have to be added throughout the following estimation of the expanded uncertainties at present.

The platinum resistance thermometer was calibrated with a precision of ± 1 mK on ITS-90 at the National Physical Laboratory, Teddington, United Kingdom in 2003. The uncertainty of the temperature measurements due to the thermometer bridge used was estimated to be ± 1 mK. The resistance of the thermometer at the triple-point temperature of water was measured periodically. The temperature of the silicone oil in the thermostatted bath was controlled within a fluctuation of ± 1 mK during the measurements of a given isotherm. And the total expanded uncertainty ($k = 2$) in the temperature measurements is 3 mK.

The precision of the two oil-operated pressure gauges used was 0.03% for $p \leqq 50$ MPa, 0.05% for 50 MPa $< p \leqq 150$ MPa, and 0.10% for $p > 150$ MPa. The pressure difference between internal and external pressures of the bellows was calibrated as a function of the bellows displacement, temperature, and pressure with a standard deviation of 0.3 kPa. The effect of hysteresis of the bellows due to compression and expansion was confirmed to be negligible. The expanded uncertainty ($k = 2$) in pressure

measurements is estimated to be 1.5 kPa ($p \leqq 7$ MPa), 0.06% (7 MPa< $p \leqq$ 50 MPa), 0.1% (50 MPa <$p \leqq 150$ MPa), and 0.2% ($p > 150$ MPa).

The inner volume of the bellows container can change from 25 to 11 cm^3, whose variation with the bellows displacement has been calibrated with the known density of water in the temperature range from 280 to 440 K at pressures up to 200 MPa. The water was de-ionized, twice distilled, and degassed more than four times by freeze-thaw cycling with liquid nitrogen. The density values of water used were calculated using the IAPWS-95 formulation [14]. The results of the calibration were correlated as a function of the bellows displacement, temperature, and pressure with a standard deviation of 0.04%. The mass of the sample was measured with a precision chemical balance (Chyo Balance: Jupiter) with an uncertainty of ±2 mg. The sample density ρ can be then calculated directly from the mass of the sample loaded and the inner volume of the bellows. The sample of propane was supplied by Takachiho Chemical Industrial Co., Ltd., Ibaragi, Japan, and its volume-fraction purity, as analyzed by the supplier, was 0.9999. Before loading the sample to the bellows, the sample was degassed using the same procedure as that for water before its use. The total uncertainty in density was calculated by applying the Gaussian error-propagation formula, which included the superimposed systematic uncertainty of the inner volume of the bellows, the random error of the correction of the inner volume of bellows, the uncertainty of the IAPWS-95 formulation, and the uncertainty of the mass of the sample. The expanded uncertainty ($k = 2$) in density measurements is estimated to be 0.11%.

4. RESULTS

We carried out a total of 63 (p, ρ, T) measurements for temperatures between 340 and 400 K at pressures up to 200 MPa. The experimental results are given in Table II. In addition, vapor pressures p^s were measured from 280 to 369 K, and the results are given in Table III. Four density measurements were also carried out at the same conditions of temperature and pressure as literature values by Reamer et al. [3], Dittmer et al. [4], Thomas and Harrison [6], and Kratzke and Müller [8], for the purpose of comparisons. The results are presented in Table IV.

5. DISCUSSION

Table IV shows a comparison of the (p, ρ, T) measurements with literature data [3, 4, 6, 8]. (p, ρ, T) data by Reamer et al. [3] and Kratzke and

Table II. Experimental Results for the Density ρ for Propane at Temperature T (ITS-90) and Pressure p

T (K)	340.000	360.000	380.000	400.000
p (MPa)		$\rho(\text{k}\cdot\text{gm}^{-3})$		
200.00	631.34	622.28	612.75	604.47
180.00	622.47	613.60	603.76	594.86
160.00	613.42	603.94	593.57	584.27
140.00	603.23	593.24	582.40	572.43
120.00	592.00	581.13	569.69	559.13
100.00	579.21	567.52	555.08	543.68
90.00	571.96	559.54	546.83	534.99
80.00	564.13	551.28	537.77	525.29
70.00	555.40	541.74	527.68	514.40
60.00	545.76	531.24	516.27	501.88
50.000	534.58	519.13	502.92	487.17
40.000	521.92	504.75	486.90	469.52
30.000	506.41	486.97	466.65	446.42
20.000	486.49	463.18	438.11	412.17
10.000	457.22	423.91	383.94	334.82
5.000	433.15	380.52		
3.000	418.08			

Table III. Experimental Results for the Vapor Pressure p^s for Propane at Temperature T(ITS-90)

T (K)	p^s(MPa)
280.000	0.5831
300.000	0.9990
320.000	1.5998
340.000	2.4322
360.000	3.5563
365.000	3.8941
367.000	4.0368
369.000	4.1844

Müller [8] agree with the present measurements within ±0.01 and ±0.03% in density, respectively. The data by Dittmer et al. [4] and Thomas and Harrison [6] agreed reasonably with the present results to within ±0.14 and ±0.15% in density, respectively.

**Table IV.**   Comparison of the Density ρ for Propane with Literature Values

T (K)	p (MPa)	$\rho(\text{kg·m}^{-3})$	Literature	$U(\%)^a$	$\varepsilon(\%)^b$	Ref.
373.124	36.207	485.82	485.07	n.a.	−0.15	[6]
373.124	32.852	479.35	480.00	0.1	0.14	[4]
373.399	30.225	473.52	473.37	n.a.	−0.03	[8]
377.567	68.95	527.84	527.81	0.2	−0.01	[3]

^{a}Experimental uncertainties reported in the literature.
^{b}Relative density difference $\varepsilon = 100\delta\rho/\rho$ of the literature values from the present results.

Figure 2 shows relative density deviations of the present measurements from the Helmholtz-type equation of state proposed by Miyamoto and Watanabe [15]. The behaviors of density values calculated from the pressure-explicit mBWR-type equation of state developed by Younglove and Ely [16] and the multi-parameter Helmholtz-type equation of state developed by Span and Wagner [17] are also included for comparisons. The new literature data (Claus et al. [10], Glos et al. [11], and Kayukawa et al. [12]) reasonably agreed with the present measurements. In the higher pressure region above 103 MPa, the behavior of calculated density values from three models (by Younglove and Ely [16], Miyamoto and Watanabe [15], and Span and Wagner [17]) and the present measurements agreed reasonably as shown in Fig. 2, although it is an extrapolated region for the three models. It was partly caused by the existence of the precise measurements of Dittmer et al. [4] in the higher pressure region up to 103 MPa. The need for improvements of the models in the higher temperature region at the middle range of pressures is demonstrated in Fig. 2.

Figure 3 shows relative pressure deviations of the present measurements from the Wagner-type vapor–pressure correlation for propane proposed by Miyamoto and Watanabe [15]. The vapor–pressure data by Reamer et al. [3], Helgeson and Sage [18], Teichmann [19], Kratzke [20], Thomas and Harrison [6], Glos et al. [11], and Kayukawa et al. [12] were also included in Fig. 3. Although our data show systematic deviations with calculated values from the correlation, most of the present measurements are well represented by the correlation within ±1.3 kPa, which is less than the experimental uncertainty, including data close to the critical temperature.
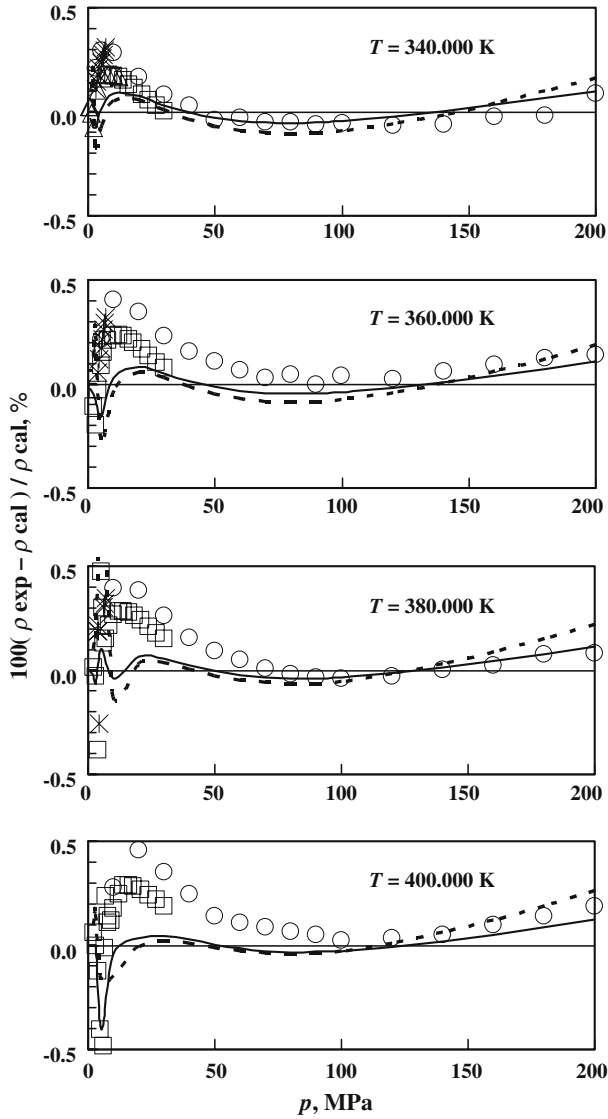
Fig. 2. Relative density deviations of the present measurements for propane from Miyamoto–Watanabe model [15]. ○, This work; ......, Younglove–Ely model [16]; – –, Span–Wagner model [17]; □, Claus et al. [10]; △, Glos et al. [11]; ∗, Kayukawa et al. [12].
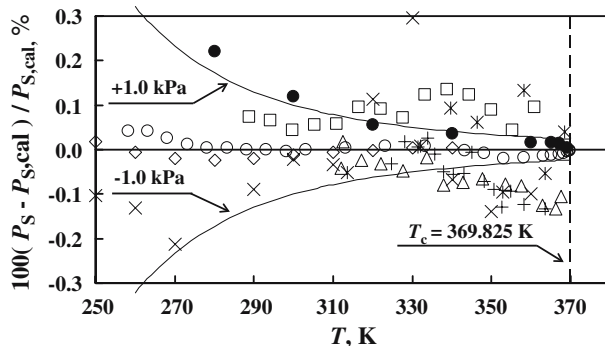
Fig. 3. Relative deviations of the experimental vapor–pressure values from the Wagner-type vapor–pressure correlation for propane proposed by Miyamoto and Watanabe [15] plotted against T, ●, This work; ∗, Reamer et al. [3]; □, Helgeson and Sage [18]; +, Teichmann [19]; □, Kratzke [20]; ○, Thomas and Harrison [6]; ◇, Glos et al. [11]; ×, Kayukawa et al. [12].

REFERENCES

1. H. Miyamoto, J. Takemura, and M. Uematsu, *J. Chem. Thermodyn.* 36:919 (2004).
2. H. Miyamoto and M. Uematsu, *J. Chem. Thermodyn.* 38:360 (2006).
3. H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.* 41:482 (1949).
4. P. Dittmer, F. Schulz, and G. Strese, *Chemie-Ing.-Techn.* 34:437 (1962).
5. J. F. Ely and R. Kobayashi, *J. Chem. Eng. Data* 23:221 (1978).
6. R. H. P. Thomas and R. H. Harrison, *J. Chem. Eng. Data* 27:1 (1982).
7. W. M. Haynes, *J. Chem. Thermodyn.* 15:419 (1983).
8. H. Kratzke and S. Müller, *J. Chem. Thermodyn.* 16:1157 (1984).
9. G. C. Straty and A. M. F. Palavra, *J. Res. Natl. Bur. Stand.* 89:375 (1984).
10. P. Claus, G. Schilling, R. Kleinrahm, and W. Wagner, Internal Report, Ruhr-Universität Bochum (2002, cited as Ref. 40 in Ref. 11).
11. S. Glos, R. Kleinrahm, and W. Wagner, *J. Chem. Thermodyn.* 36:1037 (2004).
12. Y. Kayukawa, M. Hasumoto, Y. Kano, and K. Watanabe, *J. Chem. Eng. Data* 50:556 (2005).
13. Y. Kabata, S. Yamaguchi, M. Takada, and M. Uematsu, *J. Chem.Thermodyn.* 24:785 (1992).
14. W. Wagner and A. Pruβ, *J. Phys. Chem. Ref. Data* 31:387 (2002).
15. H. Miyamoto and K. Watanabe, *Int. J. Thermophys.* 21:1045 (2000).
16. B. A. Younglove and J. F. Ely, *J. Phys. Chem. Ref. Data* 16:577 (1987).
17. R. Span and W. Wagner, *Int. J. Thermophys.* 24:41 (2003).
18. N. L. Helgeson and B. H. Sage, *J. Chem. Eng. Data* 12:47 (1967).
19. J. Teichmann, Ph. D. Dissertation (Ruhr University, Bochum, 1978).
20. H. Kratzke, *J. Chem. Thermodyn.* 12:305 (1980).