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# Isochoric ($p$–$\rho$–$T$) Measurements on Liquid and Gaseous Air from 67 to 400 K at Pressures to 35 MPa

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Comprehensive isochoric $p$–$\rho$–$T$ measurements have been carried out on liquid and gaseous air along 16 isochores at densities ranging from 2 to 32 mol · dm$^{-3}$. The air mixture has a nominal composition of $0.7812\ N_2 + 0.2096\ O_2 + 0.0092$ Ar. The $p$–$\rho$–$T$ data cover a temperature range from 67 to 400 K at pressures up to 35 MPa. Comparisons with experimental results from independent sources are presented using a fundamental equation of state based, in part, on the $p$–$\rho$–$T$ data from this study.

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**KEY WORDS:** air; density; high pressure; isochoric; mixtures; vapor.

## 1. INTRODUCTION

The investigation of the $p$–$\rho$–$T$ surface of air reported here was part of a comprehensive program at the National Institute of Standards and Technology (NIST) to determine the thermophysical properties of air. Other studies have included measurements of heat capacity [1], sound speed [2], phase equilibria [3], thermal conductivity [4], and viscosity [5]. Accurate properties for air, especially at low temperatures, are crucial in the design of hypersonic space vehicles. Although there are numerous $p$–$\rho$–$T$ data sets in the literature for air, there are none that cover as wide a temperature range as in the current study. Also, there are few liquid data at low temperatures down to the solid line. Therefore, this project was undertaken to provide $p$–$\rho$–$T$ data for air that would reduce substantially the level of uncertainty in thermodynamic properties over wide ranges of conditions, but especially at low temperatures. The experimental data from

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this study have been incorporated into the development of standard reference models and computerized databases for the calculation of the thermodynamic and transport properties of air and related mixtures containing oxygen, nitrogen, and argon.

The $p$-$\rho$-$T$ measurements of air presented here were taken along sixteen isochores spanning a range of densities from 2 to 32 mol · dm$^{-3}$. The data cover temperatures from 67 to 400 K at pressures up to 35 MPa.

## 2. EXPERIMENTS

The experimental method, apparatus, and procedures have been described in detail in previous papers [6, 7], and therefore, only a brief symmary is presented here. A gas-expansion isochoric technique was employed to measure the single-phase densities reported in this paper. In this method, a fluid of unknown density is contained in a cell of nearly fixed volume for which the volume is accurately known as a function of temperature and pressure. A series of $p$-$T$ measurements are made along a selected isochore on the sample fluid until either a maximum pressure of 35 MPa or a maximum temperature of 400 K is attained. At the end of the nearly isochoric $p$-$T$ observations, the fluid sample is expanded into large glass bulbs of accurately known volumes ranging from 1 to 21 dm$^3$ that are maintained at approximately 320 K, a temperature well above the critical temperature of the sample fluid. The density of the test fluid can then be determined based on a knowledge of the cell volume and of the compressibility factor of the fluid at the measured temperature and pressure at the expanded conditions. The compressibility factor was calculated with an extended corresponding-states model which is accurate to $\pm 0.01\%$ at the low-pressure conditions of the expanded fluid sample. Adjustments are made to account for the noxious volumes in the capillary lines and pressure gauges. A detailed description of the analysis of the experimental uncertainties involved in this technique are presented elsewhere [8]. The uncertainties in the density determination were estimated to be approximately $\pm 0.02\%$ (presented as $\pm 1\sigma$) arising from random effects and $\pm 0.05\%$ arising from systematic effects, resulting in an overall uncertainty in density of approximately $\pm 0.07\%$.

The sample cell is a cylindrical piece of pure copper containing a cavity with a volume of approximately 28.5 cm$^3$. It is suspended inside an evacuated cryostat from a thin-walled stainless-steel tube used for reflux cooling. High-resistance wire wound tightly around the cell is used to heat the cell. The cell temperature is determined with a platinum resistance thermometer (calibrated at NIST relative to the IPTS-68) embedded in a small well at the top of the cell. The temperatures were controlled and reproduced to within ±1 mK. The total uncertainties in the temperatures ranged from ±10 mK at 100 K to ±30 mK at 300 K.

Pressure measurements are made with an electronic transducer that generates a periodic signal whose frequency depends on stress applied to an oscillating quartz element. Because the frequency of the signal also varies with the temperature of the quartz element, the pressure transducer is thermally isolated in an aluminum oven thermostatted at 60°C. The pressure transducer was calibrated against an oil deadweight gauge with a certified uncertainty of ±0.01%. The overall uncertainty in the pressure measurements is approximately ±0.01% for pressures greater than 3 MPa but increases to ±0.05% at low pressures ($<1$ MPa) as a result of the transducer resolution, of the fluctuations in the temperature of the pressure transducer, and of the occasional hysteresis in the vibrational frequency of the quartz element. The precision of pressure measurements is about ±0.003%.

The gas mixtures were prepared gravimetrically in thoroughly cleaned and dried aluminium cylinders, each with a free volume of approximately 16 dm$^3$. Three cylinders of a target air mixture were prepared to provide sufficient sample for comprehensive measurements of the key thermodynamic and transport properties of air. The mixtures were prepared from pure research-grade gases that were analyzed chromatographically for impurities before us. The weighings were initially performed on an electronic load cell while filling the cylinder to optimize chances of achieving the desired mixture composition. The final weighings were made on a dual-pan analytical balance with a resolution of ±5 mg. The amount of prepared mixture sample in each cylinder was, at least, 50 mol at a pressure of approximately 7 MPa. The uncertainties in the mole fractions of the mixture components are estimated to be $\pm 4.0 \times 10^{-6}$ for $N_2$, $\pm 3.5 \times 10^{-6}$ for $O_2$, and $\pm 2.8 \times 10^{-6}$ for Ar. Two of the three cylinders of prepared air mixture were used in the current study. The compositions of these two samples are $0.78112\,N_2 + 0.20966\,O_2 + 0.00922\,Ar$ and $0.78120\,N_2 + 0.20958\,O_2 + 0.00922\,Ar$. The small difference in the composition of the two mixtures has negligible effect on the density measurements. The selected target composition for this study was taken from Jones [9], neglecting the presence of $CO_2$. The naturally occurring concentration of $CO_2$ (0.0003 mole fraction) is low enough that negligible improvements could be made to existing property models based on additional measurements on mixtures containing $CO_2$ at such low concentrations.

Since there is no stirring mechanism inside the cell to mix the sample, special care was exercised during the filling procedure to prevent phase separation of the prepared gas mixtures, that is, to ensure that the composition of the fluid inside the cell was the same as that of the gas in the supply cylinder. Before each filling of the $p$–$\rho$–$T$ cell with the air sample, the cylinder containing the prepared mixture was heated to ensure homogeneity of the mixture sample. The value of experimental density to be studied was selected, and the filling conditions ($T_f$, $p_f$) for this density were determined using a preliminary equation of state. For compressed gas experiments, we used nitrogen reflux gas to cool the cell to $T_f$, after which we used a diaphragm-type gas compressor to charge the fluid sample. When the fluid pressure reached $p_f$, the experimental volume was isolated from the charging manifold and the cell was cooled further to a temperature slightly below the first state point to be measured. A variation of the filling procedure was used for compressed liquid isochores. In these cases, the cell was filled rapidly to a desired pressure while being controlled at a temperature above the critical temperature of the mixture. Then, as the cell was cooled to a temperature below critical, the sample pressure was maintained at a level well above the critical pressure of the mixture to prevent phase separation. After filling the cell, an automated control and data acquisition system then collected a sequence of $p$–$T$ measurements of the fluid sample by heating the cell to preselected temperatures and recording the $p$–$T$ data when the sample was judged to be in equilibrium at each temperature. Additional details of the measurement procedures and automation of the apparatus have been discussed by Magee and Ely [7].

## 3. RESULTS

The experimental densities $\rho$ ($\mathrm{mol \cdot dm^{-3}}$) are presented as a function of pressure $p$ (MPa) and temperature $T$ (K; ITS-90) in Table I. In total, 286 $p$–$\rho$–$T$ state points are presented. These points were measured on a total of 16 isochoric runs with temperature intervals of 1 to 20 K. The experimental temperature measurements were made on the IPTS-68 and were converted to ITS-90 by using a table of conversions [10]. For the data in Table I, the pressure and temperature measurements are illustrated in Fig. 1.

During the course of these measurements, two nearly identical air compositions were used. Measurements along the six isochores between 6 and 16 $\mathrm{mol \cdot dm^{-3}}$ were made on air having a mole fraction composition of $0.78112\ N_2 + 0.20966\ O_2 + 0.00922$ Ar. All other measurements were made on air samples having a composition of $0.78120\ N_2 + 0.20958\ O_2 + 0.00922$ Ar. The difference of the $N_2$ and $O_2$ compositions was 0.00008 mole fraction, and less than 0.00001 for Ar. We applied a compositionally dependent model for air properties to calculate that differences of this size have a negligible influence on the densities. That is, they are less than the precision of the measurements. Furthermore, we investigated the

**Table I.** Experimental $p$–$\rho$–$T$ Data for Air:
$T$, Temperature (ITS-90); $p$, Pressure; $\rho$, Density

| $T$ (K) | $p$ (MPa) | $\rho$ (mol·dm$^{-3}$) |
|---|---|---|
| $0.781120\ N_2 + 0.20958\ O_2 + 0.00922\ Ar$ | | |
| 120.012 | 1.5427 | 1.9921 |
| 125.012 | 1.6437 | 1.9916 |
| 130.013 | 1.7432 | 1.9911 |
| 135.012 | 1.8415 | 1.9906 |
| 140.013 | 1.9387 | 1.9900 |
| 145.013 | 2.0353 | 1.9895 |
| 150.013 | 2.1312 | 1.9889 |
| 155.012 | 2.2265 | 1.9884 |
| 160.013 | 2.3213 | 1.9878 |
| 165.013 | 2.4156 | 1.9873 |
| 170.012 | 2.5096 | 1.9867 |
| 175.013 | 2.6031 | 1.9861 |
| 180.012 | 2.6964 | 1.9856 |
| 185.012 | 2.7893 | 1.9850 |
| 190.012 | 2.8817 | 1.9844 |
| 195.011 | 2.9742 | 1.9838 |
| 200.010 | 3.0662 | 1.9832 |
| 210.008 | 3.2496 | 1.9820 |
| 220.008 | 3.4322 | 1.9808 |
| 230.008 | 3.6140 | 1.9795 |
| 240.007 | 3.7952 | 1.9782 |
| 250.005 | 3.9756 | 1.9769 |
| 260.003 | 4.1554 | 1.9756 |
| 270.001 | 4.3348 | 1.9742 |
| 279.997 | 4.5136 | 1.9728 |
| 289.995 | 4.6917 | 1.9714 |
| 299.995 | 4.8695 | 1.9700 |
| 319.989 | 5.2235 | 1.9671 |
| 339.983 | 5.5756 | 1.9641 |
| 359.976 | 5.9261 | 1.9610 |
| 379.973 | 6.2751 | 1.9579 |
| 399.967 | 6.6224 | 1.9546 |
| 130.013 | 2.7910 | 4.0297 |
| 135.013 | 3.0235 | 4.0285 |
| 140.012 | 3.2510 | 4.0274 |
| 145.013 | 3.4751 | 4.0263 |
| 150.013 | 3.6966 | 4.0251 |
| 155.013 | 3.9156 | 4.0239 |
| 160.013 | 4.1326 | 4.0227 |
| 165.012 | 4.3482 | 4.0216 |
| 170.012 | 4.5622 | 4.0204 |

Table I. *(Continued)*

| $T$ (K) | $p$ (MPa) | $\rho$ ($\mathrm{mol \cdot dm^{-3}}$) |
|---|---|---|
| 175.012 | 4.7751 | 4.0192 |
| 180.011 | 4.9869 | 4.0179 |
| 185.011 | 5.1975 | 4.0167 |
| 190.011 | 5.4072 | 4.0155 |
| 195.012 | 5.6162 | 4.0142 |
| 200.011 | 5.8241 | 4.0130 |
| 210.010 | 6.2383 | 4.0104 |
| 220.010 | 6.6493 | 4.0078 |
| 230.009 | 7.0584 | 4.0052 |
| 240.007 | 7.4657 | 4.0025 |
| 250.005 | 7.8700 | 3.9998 |
| 260.002 | 8.2730 | 3.9970 |
| 270.000 | 8.4744 | 3.9942 |
| 279.998 | 9.0740 | 3.9914 |
| 289.995 | 9.4724 | 3.9885 |
| 299.996 | 9.8694 | 3.9855 |
| 319.988 | 10.6587 | 3.9795 |
| 339.984 | 11.4425 | 3.9733 |
| 359.979 | 12.2218 | 3.9670 |
| 379.973 | 12.9961 | 3.9604 |
| 399.969 | 13.7659 | 3.9537 |
| $0.78112\ N_2 + 0.20966\ O_2 + 0.00922\ Ar$ | | |
| 135.014 | 3.6770 | 6.0718 |
| 140.014 | 4.0634 | 6.0700 |
| 145.012 | 4.4397 | 6.0682 |
| 150.012 | 4.8103 | 6.0663 |
| 155.013 | 5.1768 | 6.0645 |
| 160.012 | 5.5398 | 6.0626 |
| 165.012 | 5.8999 | 6.0608 |
| 170.013 | 6.2573 | 6.0589 |
| 175.011 | 6.6126 | 6.0570 |
| 180.011 | 6.9659 | 6.0551 |
| 185.011 | 7.3176 | 6.0532 |
| 190.011 | 7.6675 | 6.0512 |
| 195.010 | 8.0157 | 6.0493 |
| 200.010 | 8.3626 | 6.0473 |
| 210.009 | 9.0526 | 6.0433 |
| 220.009 | 9.7379 | 6.0393 |
| 230.006 | 10.4190 | 6.0352 |
| 240.006 | 11.0962 | 6.0310 |
| 250.006 | 11.7698 | 6.0268 |
| 260.002 | 12.4399 | 6.0225 |

**Table I.** *(Continued)*

| $T$ (K) | $p$ (MPa) | $\rho$ ($\mathrm{mol \cdot dm^{-3}}$) |
|---|---|---|
| 270.000 | 13.1069 | 6.0182 |
| 279.998 | 13.7712 | 6.0138 |
| 289.997 | 14.4321 | 6.0093 |
| 299.996 | 15.0900 | 6.0048 |
| 319.989 | 16.3983 | 5.9956 |
| 339.984 | 17.6970 | 5.9862 |
| 359.978 | 18.9840 | 5.9765 |
| 140.014 | 4.5376 | 8.0701 |
| 145.013 | 5.0833 | 8.0676 |
| 150.013 | 5.6198 | 8.0650 |
| 155.014 | 6.1508 | 8.0625 |
| 160.012 | 6.6771 | 8.0599 |
| 165.011 | 7.2000 | 8.0573 |
| 170.011 | 7.7198 | 8.0547 |
| 175.011 | 8.2370 | 8.0521 |
| 180.011 | 8.7521 | 8.0495 |
| 185.011 | 9.2650 | 8.0468 |
| 190.013 | 9.7756 | 8.0441 |
| 195.011 | 10.2845 | 8.0414 |
| 200.010 | 10.7917 | 8.0387 |
| 210.011 | 11.8009 | 8.0333 |
| 220.009 | 12.8033 | 8.0277 |
| 230.007 | 13.7994 | 8.0221 |
| 240.006 | 14.7904 | 8.0164 |
| 250.005 | 5.7752 | 8.0107 |
| 260.005 | 16.755 | 8.0049 |
| 270.002 | 17.731 | 7.9990 |
| 280.000 | 18.700 | 7.9930 |
| 289.996 | 19.666 | 7.9870 |
| 299.995 | 20.627 | 7.9809 |
| 319.986 | 22.536 | 7.9685 |
| 339.983 | 24.429 | 7.9559 |
| 135.012 | 4.1304 | 10.158 |
| 140.012 | 4.8729 | 10.155 |
| 145.013 | 5.6027 | 10.152 |
| 150.013 | 6.3288 | 10.148 |
| 155.012 | 7.0526 | 10.145 |
| 160.012 | 7.7736 | 10.142 |
| 165.012 | 8.4929 | 10.138 |
| 170.011 | 9.2098 | 10.135 |
| 175.012 | 9.9249 | 10.131 |
| 180.011 | 10.6379 | 10.128 |
| 185.011 | 11.3484 | 10.125 |

**Table I.** *(Continued)*

| $T$ (K) | $p$ (MPa) | $\rho$ (mol · dm$^{-3}$) |
|---|---|---|
| 190.011 | 2.0564 | 10.121 |
| 195.011 | 12.7628 | 10.118 |
| 200.011 | 3.4675 | 10.114 |
| 210.009 | 4.8696 | 10.107 |
| 220.008 | 16.2642 | 10.100 |
| 230.008 | 17.651 | 10.092 |
| 240.007 | 19.030 | 10.085 |
| 250.004 | 20.400 | 10.078 |
| 260.003 | 21.764 | 10.070 |
| 270.001 | 23.120 | 10.063 |
| 279.998 | 24.469 | 10.055 |
| 289.996 | 25.811 | 10.047 |
| 299.994 | 27.146 | 10.040 |
| 319.987 | 29.797 | 10.024 |
| 135.013 | 4.2393 | 12.113 |
| 140.013 | 5.1520 | 12.109 |
| 145.012 | 6.0783 | 12.105 |
| 150.013 | 7.0109 | 12.101 |
| 155.013 | 7.9461 | 12.097 |
| 160.013 | 8.8826 | 12.092 |
| 165.013 | 9.8191 | 12.088 |
| 170.011 | 10.7554 | 12.084 |
| 175.012 | 11.6904 | 12.080 |
| 180.011 | 12.6244 | 12.075 |
| 185.011 | 13.5551 | 12.071 |
| 190.011 | 14.4856 | 12.067 |
| 195.011 | 15.4128 | 12.062 |
| 200.011 | 16.3380 | 12.058 |
| 210.009 | 18.181 | 12.049 |
| 220.010 | 20.014 | 12.040 |
| 230.007 | 21.836 | 12.031 |
| 240.006 | 23.647 | 12.022 |
| 250.003 | 25.449 | 12.013 |
| 260.002 | 27.240 | 12.004 |
| 270.000 | 29.020 | 11.995 |
| 279.999 | 30.791 | 11.986 |
| 289.995 | 32.551 | 11.977 |
| 299.992 | 34.300 | 11.968 |
| 135.013 | 4.3850 | 14.113 |
| 140.013 | 5.5334 | 14.108 |
| 145.013 | 6.7117 | 14.103 |
| 150.013 | 7.9041 | 14.098 |
| 155.014 | 9.1046 | 14.093 |

Table I. *(Continued)*

| $T$ (K) | $p$ (MPa) | $\rho$ ($\mathrm{mol \cdot dm^{-3}}$) |
|---|---|---|
| 160.014 | 10.3091 | 14.088 |
| 165.012 | 11.5171 | 14.083 |
| 170.012 | 12.8250 | 14.077 |
| 175.012 | 13.9327 | 14.072 |
| 180.010 | 15.1386 | 14.067 |
| 185.011 | 16.3430 | 14.062 |
| 190.011 | 17.545 | 14.056 |
| 195.011 | 18.744 | 14.051 |
| 200.011 | 19.940 | 14.046 |
| 210.010 | 22.323 | 14.035 |
| 220.007 | 24.692 | 14.025 |
| 230.006 | 27.046 | 14.014 |
| 240.008 | 29.385 | 14.003 |
| 250.003 | 31.709 | 13.993 |
| 260.004 | 34.019 | 13.982 |
| 135.014 | 4.7563 | 16.112 |
| 140.014 | 6.2328 | 16.106 |
| 145.012 | 7.7412 | 16.100 |
| 150.014 | 9.2700 | 16.093 |
| 155.012 | 10.8054 | 16.087 |
| 160.013 | 12.3475 | 16.081 |
| 165.011 | 13.8912 | 16.074 |
| 170.013 | 15.4344 | 16.068 |
| 175.012 | 16.978 | 16.062 |
| 180.011 | 18.517 | 16.056 |
| 185.012 | 20.056 | 16.049 |
| 190.011 | 21.589 | 16.043 |
| 195.010 | 23.118 | 16.037 |
| 200.009 | 24.643 | 16.031 |
| 210.009 | 27.675 | 16.018 |
| 220.008 | 30.687 | 16.006 |
| 230.007 | 33.678 | 15.994 |
| $0.78120\ N_2 + 0.20958\ O_2 + 0.00922\ Ar$ | | |
| 135.013 | 5.7887 | 18.177 |
| 140.013 | 7.7311 | 18.169 |
| 145.013 | 9.6916 | 18.162 |
| 150.014 | 11.6546 | 18.154 |
| 155.013 | 13.6495 | 18.146 |
| 160.013 | 15.6314 | 18.139 |
| 165.013 | 17.611 | 18.131 |
| 170.012 | 19.588 | 18.124 |

Table I. *(Continued)*

| $T$ (K) | $p$ (MPa) | $\rho$ ($mol \cdot dm^{-3}$) |
|---|---|---|
| 175.012 | 21.559 | 18.116 |
| 180.012 | 23.525 | 18.109 |
| 185.011 | 25.487 | 18.102 |
| 190.012 | 27.437 | 18.094 |
| 195.011 | 29.382 | 18.087 |
| 200.010 | 31.319 | 18.080 |
| 210.009 | 35.168 | 18.066 |
| 130.013 | 5.5634 | 20.081 |
| 135.013 | 8.0317 | 20.072 |
| 140.013 | 10.5130 | 20.063 |
| 145.014 | 12.9816 | 20.054 |
| 150.013 | 15.4484 | 20.045 |
| 155.013 | 17.937 | 20.036 |
| 160.014 | 20.422 | 20.027 |
| 165.012 | 22.890 | 20.019 |
| 170.013 | 25.350 | 20.010 |
| 175.011 | 27.806 | 20.001 |
| 180.012 | 30.244 | 19.993 |
| 185.011 | 32.670 | 19.985 |
| 190.010 | 35.083 | 19.977 |
| 125.013 | 6.2252 | 22.099 |
| 130.013 | 9.4165 | 22.088 |
| 135.014 | 12.6057 | 22.077 |
| 140.013 | 15.7885 | 22.066 |
| 145.013 | 18.953 | 22.055 |
| 150.014 | 22.110 | 22.045 |
| 155.012 | 25.250 | 22.035 |
| 160.012 | 28.364 | 22.025 |
| 165.011 | 31.462 | 22.015 |
| 170.013 | 34.540 | 22.005 |
| 115.012 | 4.5801 | 24.082 |
| 117.014 | 6.2182 | 24.077 |
| 120.012 | 8.6729 | 24.069 |
| 125.012 | 12.7443 | 24.055 |
| 130.013 | 16.790 | 24.042 |
| 135.012 | 20.804 | 24.030 |
| 140.013 | 24.787 | 24.017 |
| 145.013 | 28.736 | 24.006 |
| 150.013 | 32.651 | 23.994 |
| 115.013 | 14.1987 | 26.031 |
| 120.012 | 19.330 | 26.015 |
| 125.015 | 24.405 | 26.000 |
| 130.015 | 29.419 | 25.986 |
| 135.014 | 34.375 | 25.972 |

Table I. *(Continued)*

| $T$ (K) | $p$ (MPa) | $\rho$ (mol · dm$^{-3}$) |
|---|---|---|
| 92.008 | 1.0643 | 28.101 |
| 94.007 | 3.7798 | 28.092 |
| 96.008 | 6.4799 | 28.084 |
| 98.009 | 9.1707 | 28.076 |
| 100.010 | 11.8477 | 28.068 |
| 102.011 | 14.4966 | 28.060 |
| 104.011 | 17.139 | 28.052 |
| 106.011 | 19.763 | 28.045 |
| 108.011 | 22.371 | 28.038 |
| 110.011 | 24.945 | 28.030 |
| 112.012 | 27.522 | 28.024 |
| 114.012 | 30.078 | 28.017 |
| 116.013 | 32.626 | 28.010 |
| 82.007 | 4.3137 | 30.083 |
| 84.007 | 7.7745 | 30.072 |
| 86.008 | 11.2022 | 30.062 |
| 88.009 | 14.6065 | 30.053 |
| 90.008 | 17.972 | 30.043 |
| 92.008 | 21.320 | 30.034 |
| 94.008 | 24.647 | 30.025 |
| 96.008 | 27.937 | 30.017 |
| 98.009 | 31.212 | 30.008 |
| 100.009 | 34.463 | 30.000 |
| 67.005 | 3.3771 | 32.215 |
| 68.007 | 5.6449 | 32.208 |
| 69.007 | 7.8956 | 32.202 |
| 70.007 | 10.1350 | 32.195 |
| 71.007 | 12.3681 | 32.189 |
| 72.007 | 14.5893 | 32.183 |
| 73.007 | 16.779 | 32.177 |
| 74.007 | 18.980 | 32.171 |
| 76.007 | 23.344 | 32.160 |
| 78.008 | 27.666 | 32.149 |
| 80.009 | 31.953 | 32.138 |

dependence of the density on the slightly different compositions of the two samples used in this study by measuring $p$–$\rho$–$T$ data at 4 and at 18 mol · dm$^{-3}$ on samples from each of the supply cylinders. The densities determined at corresponding points for these two isochoric runs differed by less than 0.01 %, which is within the precision of our method.

Figures 2 and 3 depict regions of temperature and pressure covered in other investigations of the air $p$–$\rho$–$T$ surface [11–19], along with the

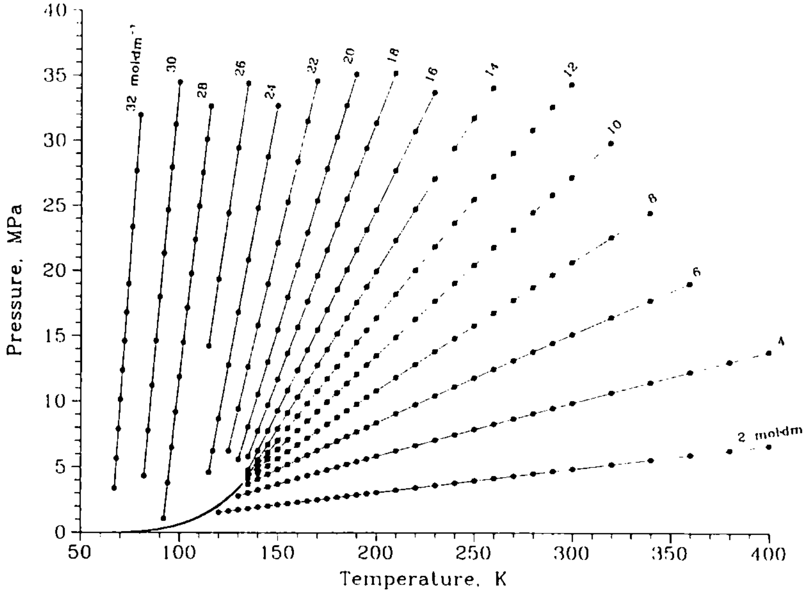

**Fig. 1.** Isochoric $p$-$\rho$-$T$ data for air collected in this study. Dew-bubble envelope and lines are depicted to guide the eye.

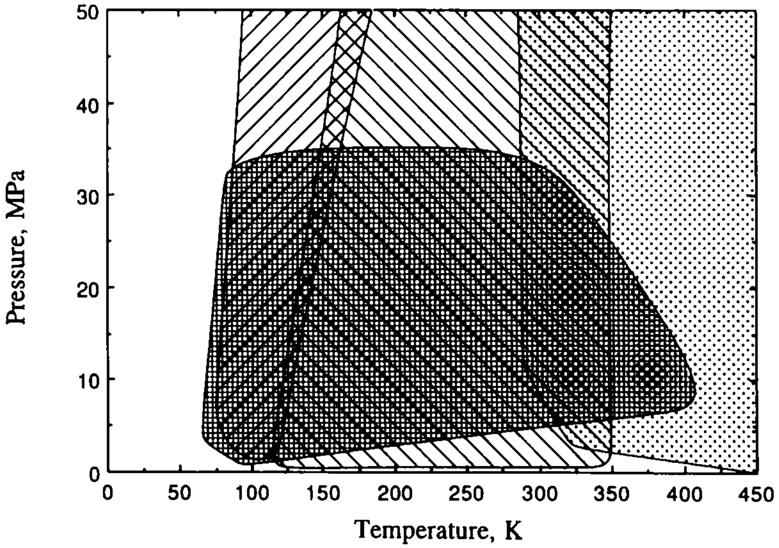

**Fig. 2.** Ranges of pressure and temperature covered by $p$-$\rho$-$T$ studies of air. This work (▦); Michels et al. [13, 14] (▨); Kozlov [16] (☐); Vasserman et al. [19] (▒).

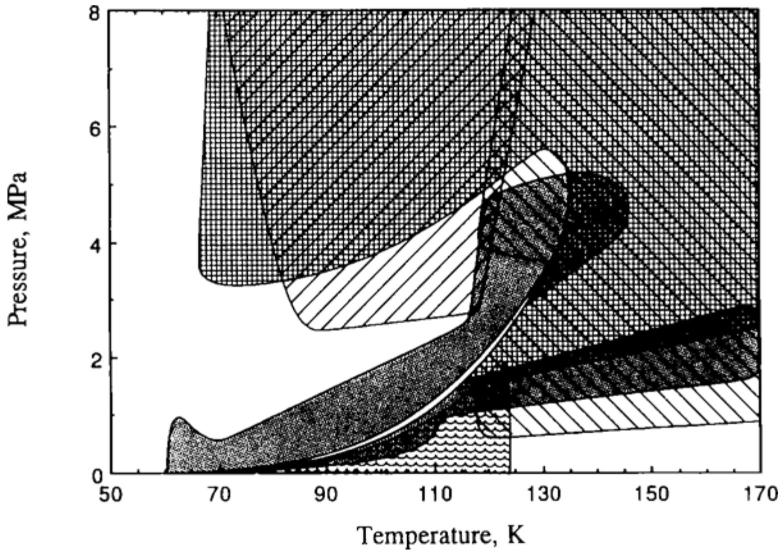

**Fig. 3.** Ranges of pressure and temperature close to saturation covered by *p–ρ–T* studies of air. This work (▦); Michels et al. [13, 14] (░); Romberg [17] (▒); Blanke [18] (☐); Vasserman et al. [19] (▨).

results from the current study. As noted from these figures, the current study extends the available data to lower temperatures than were published prior to this work. In addition, the current results overlap the pressures and temperatures of the previous studies. Hence, comparisons of the measured densities may be carried out for the published results.

The first step to be taken when doing a comparison of results is to select a calculation procedure which is to be used as the baseline. Two models which can be used to calculate the thermodynamic properties of air have been developed. The first is an extended corresponding states model, NIST14, which has been developed at NIST to predict the thermodynamic properties of multicomponent mixtures [20]. NIST14 has been successfully applied to predicting properties of industrially important mixtures, such as carbon dioxide + hydrocarbons mixtures. Because the components of air were included in this general mixture model, its capabilities can be tested against the experimental results of this study. The other model is an equation-of-state model, AIRPROPS 5.0. [21], which has been developed as part of the current NIST project on air properties. Much of the modeling work was done at the Center for Applied Thermodynamic Studies at the University of Idaho. The equation of state for air used in AIRPROPS 5.0 was developed by fitting selected published thermodynamic property data and was further optimized by fitting the $(p, \rho, T)$ results of this study, as well as recently measured heat capacities and sound speeds from this laboratory.

The performance of the two models is compared with the experimental data in Figs. 4–6. Outside the extended critical region, both models give densities quite close to the experimental values; the calculated values from AIRPROPS 5.0 are generally within ±0.1% of the data while those of NIST14 agree within about ±0.2%. Exceptions to this general level of agreement occur at some points close to the saturation boundary. The predictions of NIST14 near the vapor saturation boundary exhibit errors of up to ±0.4% which decrease rapidly with increasing temperature along an isochore. The NIST14 predictions can exhibit a small discontinuity at low densities, although the results extrapolate correctly to the ideal gas limit. This anomaly is apparent in the first graph in Fig. 4, where the predictions on the 2 mol · dm$^{-3}$ isochore show a discontinuity of −0.3% near 300 K. A line of discontinuities in the model is present for temperatures up to 800 K; future refinements in the NIST14 database are expected to reduce these small discontinuities further. The other exception to the general level of agreement is in the extended critical region from 10 to 16 mol · dm$^{-3}$ at temperatures to 170 K. The optimized equation of state of AIRPROPS 5.0 is still within ±0.1% of the experimental values, but the NIST14 calculations diverge from the data in this region. None of the NIST14 deviations exceed ±0.4%, which is within the nominal uncertainty of the predictive model.

Density data from the eight published sources [11–19] have been compared with values calculated with AIRPROPS 5.0. This model was developed by fitting most of the available thermodynamic data for air, including those from this study, by applying weights during the optimization procedure. A summary of the results appears in Table II, where the tabulated quantities %AAD (percentage average absolute deviation) and %bias (percentage bias) are defined as follows:

$$\%\mathrm{AAD} = \frac{100}{n} \times \sum_{i}^{n} \frac{|\rho_{\mathrm{exp}}(T_i, p_i) - \rho_{\mathrm{AIRPROPS}}(T_i, p_i)|}{\rho_{\mathrm{AIRPROPS}}(T_i, p_i)} \tag{1}$$

$$\%\mathrm{bias} = \frac{100}{n} \times \sum_{i}^{n} \frac{\rho_{\mathrm{exp}}(T_i, p_i) - \rho_{\mathrm{AIRPROPS}}(T_i, p_i)}{\rho_{\mathrm{AIRPROPS}}(T_i, p_i)} \tag{2}$$

Here $\rho_{\mathrm{exp}}(T_i, p_i)$ and $\rho_{\mathrm{AIRPROPS}}(T_i, p_i)$ denote the densities measured experimentally and computed by AIRPROPS 5.0, respectively, at the state point $(T_i, p_i)$. The sums are over $n$ data points quoted in each source. Of the other sources of $p$–$\rho$–$T$ data that were examined, only three specified the compositions of the air samples: those of Blanke [18], Kozlov [16],

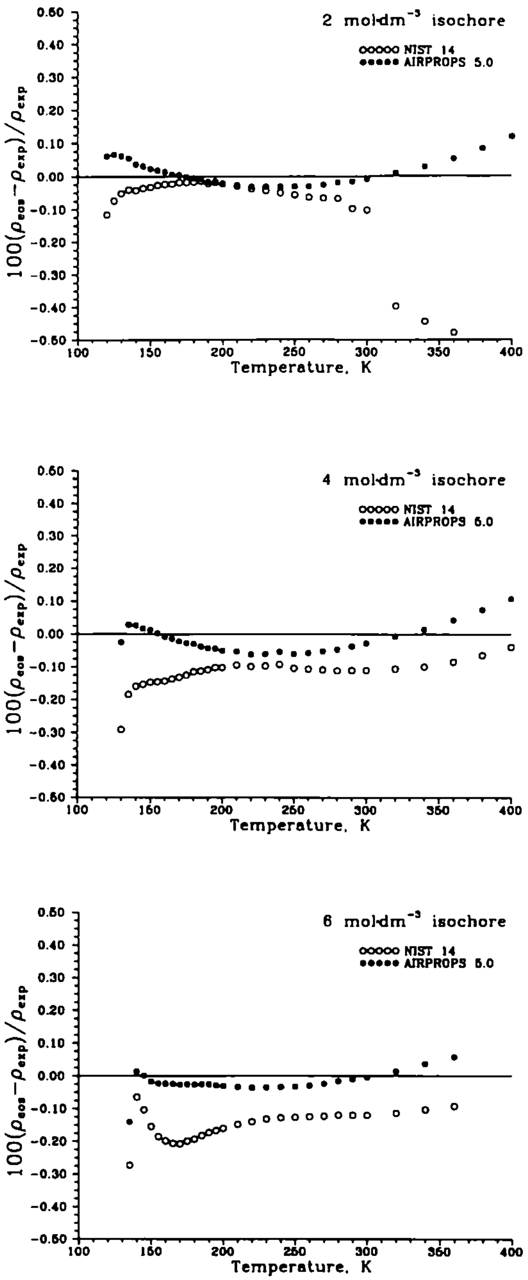

Fig. 4. Comparison of the density predictions of NIST14 and AIRPROPS 5.0 with the *p*–ρ–*T* data of this study from 2 to 6 mol · dm$^{-3}$.

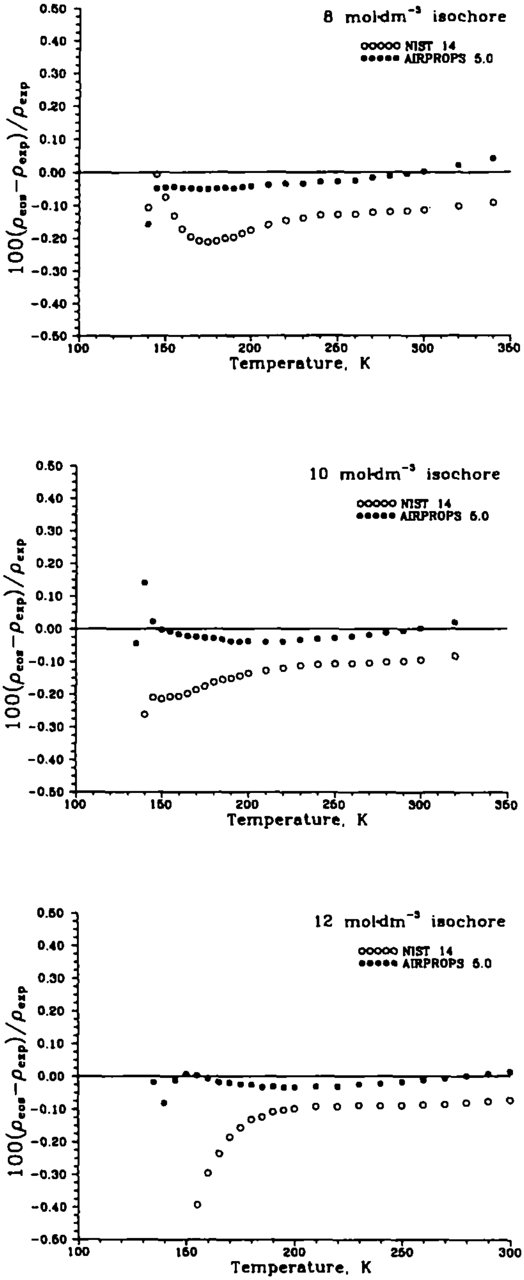

Fig. 5. Comparison of the density predictions of NIST14 and AIRPROPS 5.0 with the $p$-$\rho$-$T$ data of this study from 8 to 12 mol·dm$^{-3}$.

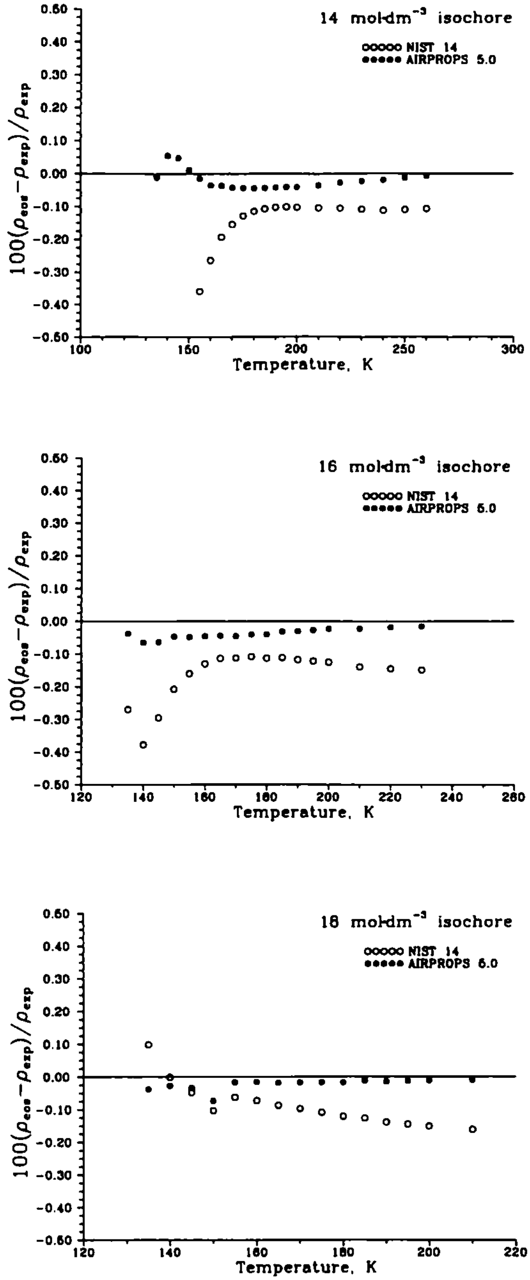

Fig. 6. Comparison of the density predictions of NIST14 and AIRPROPS 5.0 with the $p$–$\rho$–$T$ data of this study from 14 to 18 mol · dm$^{-3}$.

**Table II.** Comparison of Experimental Densities for Air with Densities Calculated Using AIRPROPS 5.0 [21]

| Source (number of points compared) | Year | Range | Composition ($N_2$, $O_2$, Ar, $CO_2$) mole fraction | Comparison with AIRPROPS 5.0 | |
|---|---|---|---|---|---|
| | | | | %AAD | %bias |
| Holborn & Schultze [11] (42 points) | 1915 | 273-473 K<br>2-10 MPa | Not given | 0.020 | 0.010 |
| Penning [12] (62 points) | 1923 | 128-293 K<br>2.5-6.2 MPa | Not given | 0.070 | 0.025 |
| Michels et al. [13, 14] (356 points) | 1954 | 120-350 K<br>0.5-230 MPa | Not given | 0.098 | −0.044 |
| Rogovaya & Kaganer [15] (10 points) | 1960 | 173-273 K<br>1.9-11 MPa | Not given | 0.088 | −0.050 |
| Kozlov [16] (347 points) | 1968 | 290-870 K<br>1-72 MPa | (0.7814, 0.2090, 0.0093, 0.0003) | 0.060 | −0.020 |
| Romberg [17] (124 points) | 1971 | 84-120 K<br>0.02-2.0 MPa | (0.7816, 0.2091, 0.0093, 0.0000) | 0.020 | 0.013 |
| Blanke [18] (110 points) | 1973 | 60-170 K<br>0.01-5 MPa | (0.7841, 0.2066, 0.0093, 0.0000) | 0.369 | −0.253 |
| Vasserman et al [19] (109 points) | 1976 | 77-200 K<br>2.6-60 MPa | Not given | 0.062 | −0.008 |
| This work (286 points) | — | 67-400 K<br>1-35 MPa | (0.78112, 0.20966, 0.00922, 0.0000)<br>(0.78120, 0.20958, 0.00922, 0.0000) | 0.039 | 0.025 |

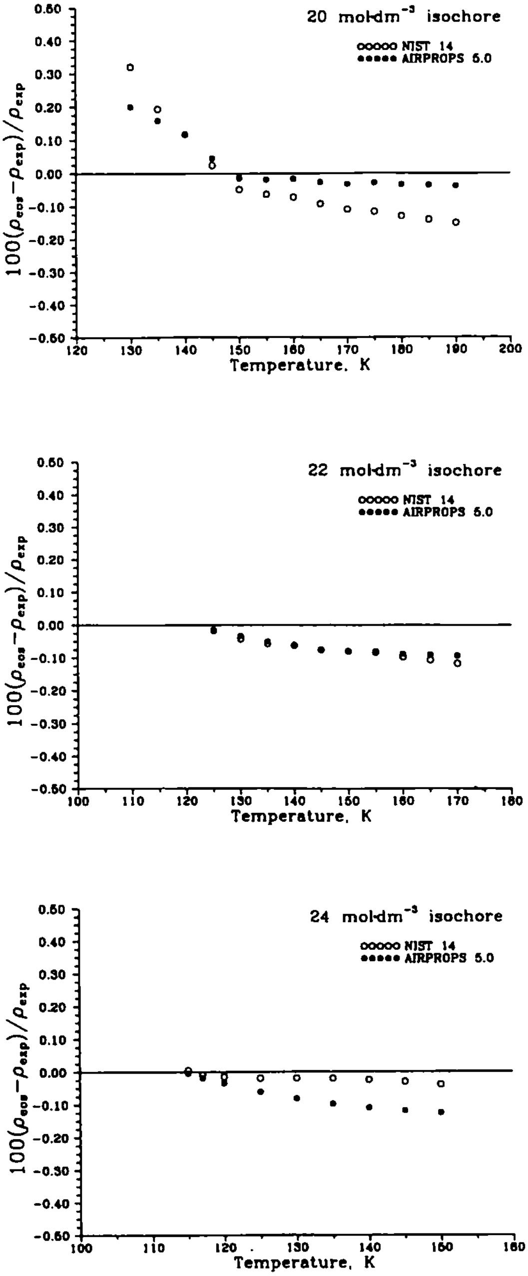

Fig. 7. Comparison of the density predictions of NIST14 and AIRPROPS 5.0 with the $p$-$\rho$-$T$ data of this study from 20 to 24 mol·dm$^{-3}$.

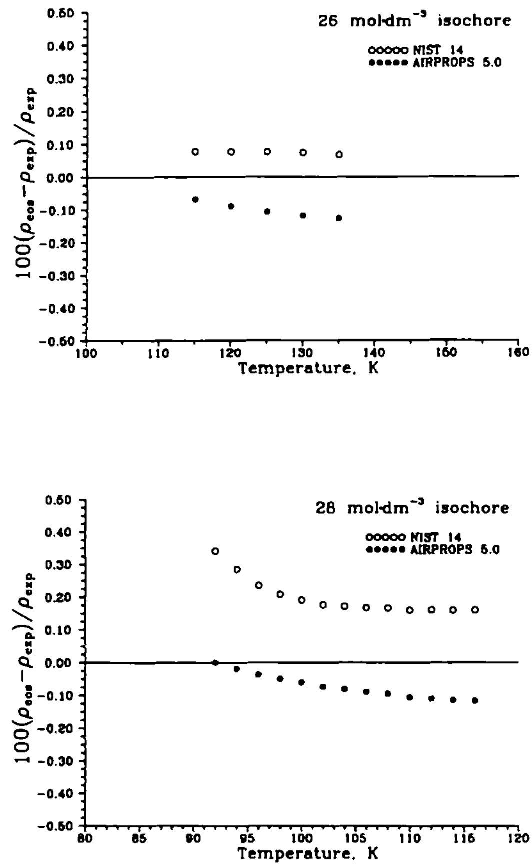

Fig. 8. Comparison of the density predictions of NIST14 and AIRPROPS 5.0 with the $p$-$\rho$-$T$ data of this study from 26 to 28 mol·dm$^{-3}$.

and Romberg [17]. However, all eight data sets were compared with AIRPROPS 5.0 by assuming the composition of the air samples to be $0.7812\ N_2 + 0.2096\ O_2 + 0.0092\ Ar$. The critical point for this composition of the ternary air mixture, as reported in Ref. 21, is $(p_c, \rho_c, T_c) =$ [3.786 MPa, 11.83 mol·dm$^{-3}$, 132.53 K (ITS-90)].

The density measurements of this study agree closely (AAD = 0.039%) with AIRPROPS 5.0 and show very little bias (0.025%) from the predictions. Examination of Table II reveals that seven of the eight sources of $p$-$\rho$-$T$ data are in good agreement (within ±0.1%) with AIRPROPS's predictions. The bias of the published data was found to be less than ±0.05%. Only the data of Blanke [18] showed a somewhat larger average

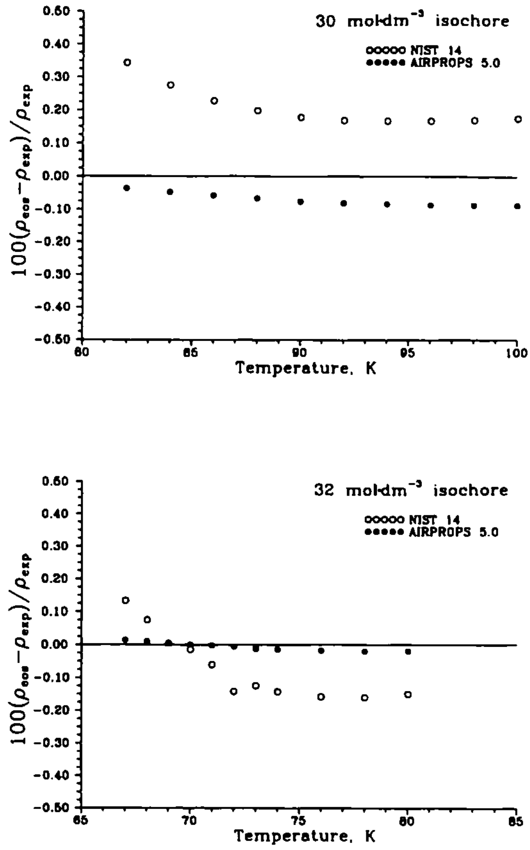

**Fig. 9.** Comparison of the density predictions of NIST14 and AIRPROPS 5.0 with the $p$–$\rho$–$T$ data of this study from 30 to 32 mol · dm$^{-3}$.

deviation (0.369%). However, this is due to a large fraction of the data falling close to the vapor saturation boundary. It is likely that AIRPROPS 5.0 expects some of these conditions to be in the two-phase region. The data of Blanke, at temperatures several degrees higher than saturation, agree with AIRPROPS 5.0 within about ±0.05%. In summary, the comparisons with AIRPROPS 5.0 indicate that there is good agreement of the densities from this work with those from published studies.

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