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Density Equation for Saturated ^{3}He

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A density equation for saturated vapor and liquid ^{3}He is presented based on 205 experimental measurements for temperatures greater than 0.2 K collected after a careful survey of the literature. The average deviation of the densities predicted by the equation against the experimental values is 0.39%. There are only 16 points with deviations larger than 1%. This equation is valid for both liquid and vapor densities of ^{3}He up to the critical temperature of 3.3157 K. The form of the equation satisfies known scaling laws approaching the critical point, with $\beta = 0.3653$. In the low-density limit, the vapor curve of our equation matches smoothly to the published virial equation density at a temperature of 1.62 K and at the saturation pressure. The rectilinear density deviates from the critical density by less than 0.28% down to 0.48 K.

KEY WORDS: equation of state; ^{3}He; saturated density.

1. INTRODUCTION

Since the middle of the 20th century, much research has focused attention on the properties of ^{3}He, a quantum fluid at low temperatures. A project to establish a database for the thermodynamic and transport properties of gaseous and liquid ^{3}He is being carried out in the Cryogenics Laboratory, Zhejiang University, with cooperation of Cryodata Inc. As an important step of the project, this paper presents an accurate saturated density equation for both liquid and vapor over a wide range from 0.2 K to the critical point at 3.3157 K. The equation uses the ITS-90 temperature scale.

The saturation behavior of this expensive isotope of helium was one of the first subjects investigated when ^{3}He became available to cryogenics laboratories. The vapor-pressure equation was studied in several papers,

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and finally the form presented by Sherman et al. [1] was adopted to define the 1962 temperature scale. Similarly, many experimental and theoretical research activities have been completed on the density of the saturated liquid and vapor of ^{3}He. Publications relevant to this work are discussed in the next section. It is necessary to point out that all of the above mentioned equations use older temperature scales (T_{58}, T_{62}, or even earlier), and the density equations are restricted to relatively narrow temperature regions. Also, the systematic errors and the measurement uncertainties are different, and some equations are not intended to be accurate in the near-critical region, especially at the critical point.

2. DATA SOURCES

The authors have collected and reviewed the literature concerned with the density of saturated liquid and vapor ^{3}He. In 1949, Grilly et al. [2] measured the differences between liquid and vapor densities of ^{3}He between 1.27 and 2.79 K. In the absence of saturated vapor density data, they estimated the absolute values of liquid densities by using the law of rectilinear diameters, and finally obtained 7 smoothed approximate density values for both liquid and vapor ^{3}He.

In 1954, Kerr [3] measured the saturated liquid and vapor densities of ^{3}He by a direct method in the temperature range from 1.3 to 3.2 K, and obtained 15 measurements of the saturated- liquid and 12 measurements of the orthobaric-vapor densities. The empirical equation from Ref. 3, $\rho = A_0 + BT \pm (A_0^2 + CT^2 + DT^3)^{1/2}$($A_0 = 0.041173\,\mathrm{g{\cdot}cm^{-3}}$, $B = 4.14 \times 10^{-5}\,\mathrm{g{\cdot}cm^{-3}} \cdot K^{-1}$, $C = -3.3015 \times 10^{-6}\,\mathrm{g^2{\cdot}cm^{-6}{\cdot}K^{-2}}$, and $D = -4.1876 \times 10^{-5}\,\mathrm{g^2{\cdot}cm^{-6}{\cdot}K^{-3}}$), represents the experimental data with deviations of about 0.3% for the liquid phase from 1.0 to 3.1 K and about 2% for the vapor phase between 1.6 and 3.1 K. From this equation, Kerr evaluated 14 values of density for both the saturated liquid and vapor at temperatures from 1.0 to 3.3 K. At low vapor densities, it appears that the equation tends to give values that are too high. Kerr suggested the use of the virial equation to give more reliable vapor-density values below about 1.6 K.

In 1957, Peshkov [4] reported six reliable observations of density for both saturated liquid and vapor ^{3}He. In 1960, Sherman and Edeskuty [5] made accurate $P - V - T$ measurements for liquid ^{3}He from 0.98 to 3.32 K and from the saturation pressure to the melting pressure. They gave a table for saturated liquid densities of ^{3}He at temperatures from 0.8 to 3.0 K, totaling 23 points. During the next year, it was mentioned in the literature [6, 7] that Sherman and Edeskuty had redetermined the volume of their cell, with the result that all reported volumes should be reduced by 0.3%.

In 1962, Kerr and Taylor [7] measured directly the molar volume of liquid ^{3}He under its own vapor-pressure over the temperature range from 0.16 to 1.8 K, with 80 of the observations below 0.7 K. Their summary equation in the temperature range from 0.17 to 1.9 K is $V_m = \sum_0^n p_n T^n$ where $p_0 = 36.8346\,\mathrm{cm^3{\cdot}mol^{-1}}$, $p_1 = 0$, $p_2 = -2.29985\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-2}}$, $p_3 = 5.79318\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-3}}$, $p_4 = -5.51920\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-4}}$, $p_5 = 2.54295\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-5}}$, and $p_6 = -0.44434\,\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-6}}$. They presented a table of the molar volumes at even temperature intervals as calculated from this fitted equation. Molar volumes above 1.8 K derived from the corrected data of Sherman and Edeskuty [5] have been included; altogether 67 points are available from this source.

In 1965, when Sherman [8] studied the behavior of ^{3}He in the critical region, he measured 23 isochores of ^{3}He with densities ranging from 0.015 to $0.066\,\mathrm{g{\cdot}cm^{-3}}$ and presented a table for the densities of ^{3}He along the coexistence curve at 14 temperatures in the range from 2.4 to 3.3 K

In 1970, Wallace and Meyer [9] provided liquid and vapor densities ρ_L and ρ_G at nine temperatures on the coexistence curve. Based on these data, they obtained ^{3}He critical parameters, $T_c = 3.3105\,\mathrm{K}$, $P_c = 114723.898\,\mathrm{Pa}$, and $\rho_c = 0.04145\,\mathrm{g{\cdot}cm^{-3}}$.

In 1973, by measuring the capacitance of a parallel-plate capacitor filled with ^{3}He as a function of temperature and pressure, Chase and Zimmerman [10, 11] determined the dielectric constant of ^{3}He along 28 isotherms between 3 K and the critical temperature for both saturated liquid and vapor. Then, assuming the Clausius–Mossotti relation holds, they calculated the density along these same trajectories. Their saturation densities from 3.2 K to the critical point were fitted to the equation$\left|\frac{\rho-\rho_c}{\rho_c}\right| = A\left(\frac{T_c-T}{T_c}\right)^\beta$ with parameters $T_c = 3.30947 \pm (5 \times 10^{-5})\,\mathrm{K}$, $\rho_c = 0.041341 \pm (5 \times 10^{-6})\,\mathrm{g{\cdot}cm^{-3}}$, $A = 1.323 \pm 0.004$, and $\beta = 0.3625 \pm 0.0010$.

The above eight experimental data sources of density on the saturated curve of ^{3}He are listed in Table I for clarity. Together they cover the temperature range from 0.2 K to the critical temperature 3.3157 K. Reliable data in the near-critical region from Wallace [9] and Chase [11] help to stabilize the equation and improve its accuracy.

We eliminated evidently erroneous data from the collected total of 239 experimental measurements. From Fig. 1, we can see that the early data given by Grilly et al. [2] deviate significantly from subsequent data; these data were not included in our least-squares fit. In addition, some data near the critical point with large deviations (see the magnified figure in Fig. 1.) were also eliminated. Finally, 205 data points were left for use in the final fit.

Table I. Density or Specific Volume of Saturated Vapor and Liquid ^{3}He

Source of data	Temperature range (K)	Phase and number of observations
Grilly et al. (1949) [2]	1–3.34	Liquid and vapor (14)
Kerr (1954) [3]	1–3.3	Liquid and vapor (27)
Peshkov (1957) [4]	1.4–3.29	Liquid and vapor (12)
Sherman & Edeskuty (1960) [5]	0.8–3	Liquid (23)
Kerr & Taylor (1962) [7]	0.2–3.2	Liquid (57)
Sherman (1965) [8]	2.4–3.324	Liquid and vapor (28)
Wallace & Meyer (1970) [9]	3.0–3.310	Liquid and vapor (34)
Chase & Zimmerman (1973) [11]	3.2–3.309	Liquid and vapor (43)

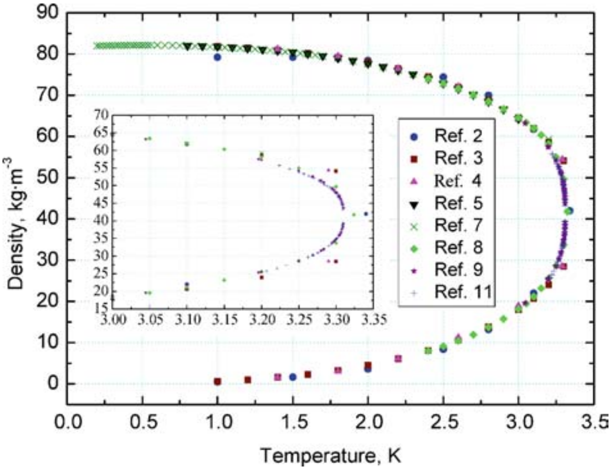

Fig. 1. Experimental data plot; magnified figure is used to show the near-critical density distribution.

3. TEMPERATURE SCALES

Most of the measurements use older temperature scales, such as T_{48} or T_{58}. In this paper, all of them were converted to the ITS-90 [12, 13] temperature scale. The conversion process to the new temperature scale is shown in Fig. 2. A computer program has been written for this function.

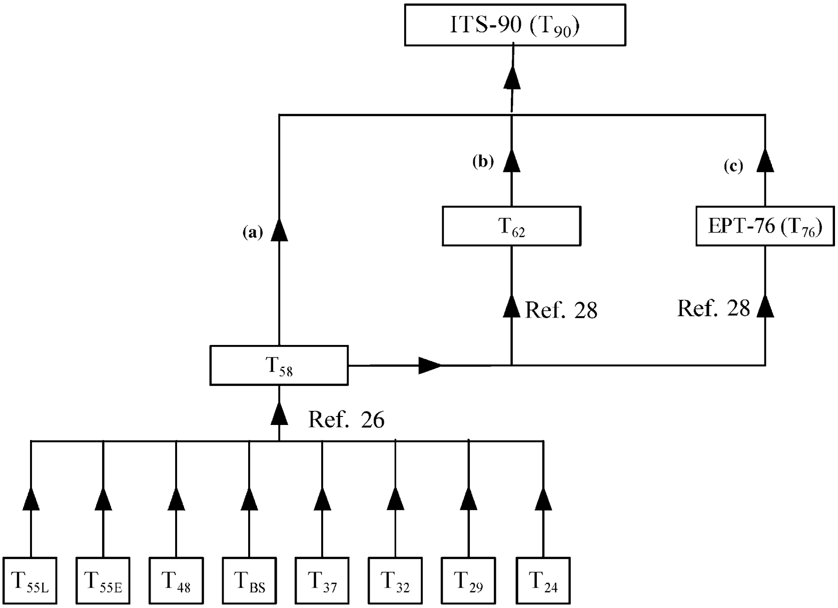

Fig. 2. Flowchart for conversion of old temperature scales to ITS-90. (a) By the ^{4}He vapor-pressure equations in Refs. 13 and 27 (T_{90} and T_{58}, respectively). (b) By the ^{3}He vapor-pressure equations in Refs. 13 and 1 (T_{90} and T_{62}, respectively). (c) By the ^{4}He vapor-pressure equations in Refs. 13 and 15 (T_{90} and T_{76}, respectively).

4. CRITICAL POINT AND NEAR-CRITICAL REGION

The critical point is very important for the development of the saturated density equation of ^{3}He. Table II gives a brief review for the critical parameters since 1949. The critical values given by Sherman in 1965 were used to define the 1962 temperature scale, but after that, new values came to be more and more precise and accurate. In the 10 years between about 1965 and 1975, research on the thermodynamic properties of pure fluids in the region of the liquid–vapor critical point has made great progress, because of the impetus provided by new scaling hypotheses and theoretical studies of the critical exponents [22]. Both Chase et al. [14] in 1973 and Behringer et al. [21] in 1976 did specific measurements and theoretical studies on the properties of ^{3}He in the near-critical region. It is reasonable to believe that new ^{3}He experimental data from Refs. 20 and 21 have avoided possible systematic errors found in earlier work. Assuming that the 0.0005 and 0.0008 values are accurate measures of the individual error estimates, a purely statistical summary would combine 3.3093 and 3.3086 K to give a mean value of 3.3090 K, which is reasonably consistent

Table II. Brief Review of the Critical Parameters of ^{3}He

Year	Publication	T_c (K)	ρ_c ($g{\cdot}cm^{-3}$)	P_c (Pa)	β
1949	Sydoriak et al. [16]	3.34	0.041	116657.072	
1950	Abraham et al. [17]	3.35 ± 0.02		118656.908 ± 2666.447	
1965	Sherman [8]	3.324 ± 0.0018	0.0418 ± 0.001	116390.428 ± 199.984	0.48 ± 0.02
1965	Chase & Zimmerman [18]	3.3245 ± 0.005	0.04131		
1967	Zimmerman & Chase [10]	3.3095	0.04134		0.362
1970	Wallace & Meyer [9]	3.3105	0.04145	114723.898	0.361
1970	Scott [19]	3.3095	0.041341		0.332
1972	Brow and Meyer [20]	3.3092 ± 0.0006			
1973	Chase & Zimmerman [14]	3.3093 ± 0.0005	0.041191 ± 0.00013	114586.576 ± 39.997	
1975	Behringer et al. [21]	3.3086 ± 0.0008		114657.237 ± 133.322	

with both. The same statistical question could be applied to the critical pressure. These numbers are more likely to be correct than would either Chase or Behringer by themselves. After converting the temperature to the ITS-90 scale, the critical parameters adopted by this paper are $T_c = 3.3157\,\mathrm{K}$, $\rho_c = 41.191\,\mathrm{Kg{\cdot}m^{-3}}$, and $\beta = 0.3653$, which differ considerably from values of Sherman [8].

5. DENSITY EQUATION FOR SATURATED ^{3}He

Following the work of Kerr [3, 7] and Zimmerman [10], a dimensionless form for the density equation was selected;

$$\rho/\rho_c = 1 \pm (c_1\tau^{\beta} + c_2\tau^{1+\beta} + c_3\tau^{2+\beta} + c_4\tau^{3+\beta}) + c_5\tau + c_6\tau^2 \qquad (1)$$

where the dimensionless parameter $\tau = (T_c - T)/T_c$. T_c is the critical temperature, ρ_c is the critical density, c_1 to c_6 are the coefficients obtained by least-squares regression, and β is a critical index to describe the density dependence near the critical point. The sign "±" is used to distinguish the liquid and vapor branches; "+" is for liquid and "−" is for vapor. This wide range form has not been previously published, although it has been used in recent work on ^{4}He [23]. In this dimensionless form, the deviations caused by the different temperature scales will affect our results only negligibly, although the old temperature scales have been converted to ITS-90. A nonlinear least-squares fit has been applied to Eq. (1) based on the selected 205 experimental measurements. Table III lists the obtained coefficients for Eq. (1).

6. STATISTICS FOR THE SATURATED DENSITY EQUATION

The statistical results of the nonlinear regression are shown in Table IV. The differences between the observed and calculated saturated densities are shown in Fig. 3, where the dashed lines enclose the limits of ±1% in density. Only 16 observations, most of them in the near-critical region, fall outside of this range, but all are within ±2%. The average and maximum relative errors of all data are 0.39 and 1.99%, respectively. Figure 4 shows the 239 experimental measurements of the density of saturated vapor and liquid ^{3}He and the curve generated by Eq. (1) of this work.

7. DISCUSSION AND ANALYSIS

The dashed curves in Figs. 5 and 6 represent the vapor densities as calculated from the ideal-gas law and those calculated from the density

Table III. Coefficients for Eq. (1)

Coefficient	Value	Standard dev.
c_1	1.337473	0.0031
c_2	−0.0267	0.0282
c_3	−0.5883	0.0683
c_4	0.27223	0.0481
c_5	0.007466	0.0059
c_6	−0.012583	0.0088
T_c(K)	3.3157	
ρ_c(kg·m^{-3})	41.191	
β	0.3653	

Table IV. Technical Results of Regression

Number of observations	205
Final sum of deviations (kg·m^{-3})	0.237
Standard error of estimate	0.0054
Average deviation (kg·m^{-3})	0.003
Maximum deviation for any observation (kg·m^{-3})	0.0275
Average relative deviation	0.39%
Maximum relative deviation	1.99%
Number of points with relative deviation larger than 1%	16

form of the virial equation of state in closed form involving only the second virial coefficients. The density virial equation gives imaginary values above about 2.7 K. This indicates that the vapor densities will be better represented by the density virial equation using at least the third virial coefficient. The values used for the second virial coefficient in the calculations are obtained from the calculations of Hurly and Moldover [24].

The curves of the $PV = RT$ equation are always under the other two curves. In the temperature range of 1.48 – 1.72 K, the curve of the virial equation and the vapor curve of Eq. (1) agree very well and cross at a temperature of about 1.62 K. Table V gives the densities and the derivatives calculated by Eq. (1) and the virial equation. It can be noticed that these two curves match each other well in this region. According to Fig. 6, a magnification of Fig. 5. at low temperatures, the curve of Eq. (1) deviates from the curves of the virial equation and ideal-gas equation. We

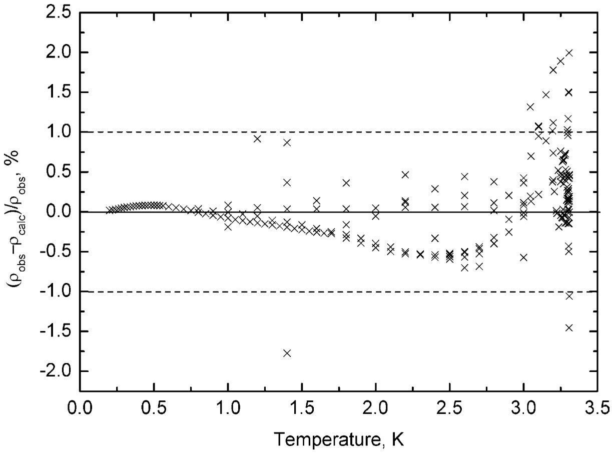

Fig. 3. Distribution of relative deviations.

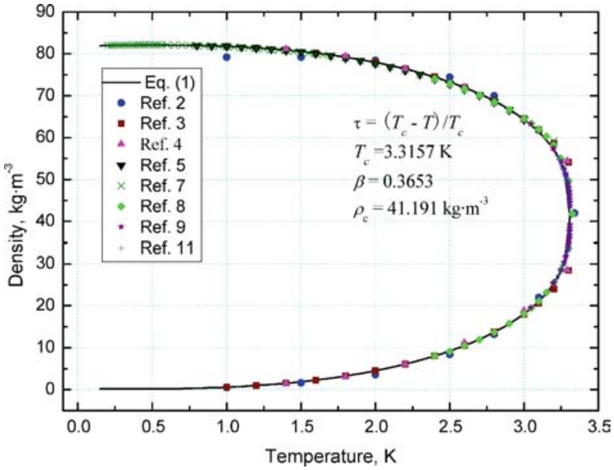

Fig. 4. Density of saturated ^{3}He curve, data, and Eq. (1).

suggest using the virial equation to give more reliable vapor-density values below about 1.62 K.

The above lower limit for the vapor branch of Eq. (1) probably does not apply to the liquid branch. Our purely statistical tests support a lower limit of 0.2 K for the liquid. We note that the observed bulk liquid thermodynamics indicate that the thermal expansivity should remain positive to temperatures at least as low as 0.2 K [25] (and probably lower).

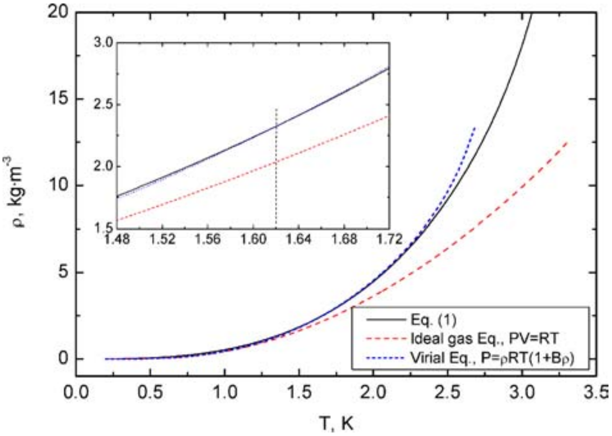

Fig. 5. Comparison of the vapor curve of our density equation with the ideal gas equation and the virial equation.

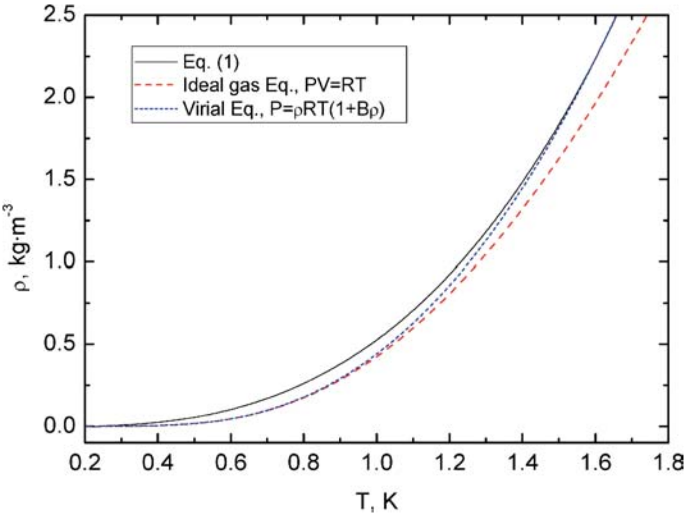

Fig. 6. Magnification of Fig. 5. in the temperature range from 0.2 to 1.8 K.

However, Eq. (1) predicts the derivative $d\rho/dT > 0$ when $T < 0.48$ K. This latter temperature thus provides another estimate for the lower limit to validate the fitted curve. On the other hand, from 0.48 to 0.2 K, the magnitude of $d\rho/dT$ remains very small, and the calculated density decreases

Table V. Density and Its Derivatives Calculated by Eq. (1) and the Virial Equation

T(K)	$\rho_{\mathrm{Eq(1)}}$ (kg·m^{-3})	$d\rho_{\mathrm{Eq(1)}}/dT$	ρ_{virial} (kg·m^{-3})	$d\rho_{\mathrm{virial}}/dT$	$(\rho_{\mathrm{Eq.(1)}} - \rho_{\mathrm{virial}})/\rho_{\mathrm{virial}}$ (%)	$\frac{d\rho_{\mathrm{Eq(1)}}/dT - d\rho_{\mathrm{virial}}/dT}{d\rho_{\mathrm{virial}}/dT}$ (%)
1.48	1.75429	3.64894	1.73096	3.81687	1.35	−4.40
1.50	1.82829	3.75274	1.80833	3.92023	1.10	−4.27
1.52	1.90439	3.85827	1.88778	4.02503	0.88	−4.14
1.54	1.98261	3.96558	1.96934	4.13134	0.67	−4.01
1.56	2.06300	4.07469	2.05304	4.23920	0.49	−3.88
1.58	2.14559	4.18562	2.13892	4.34866	0.31	−3.75
1.60	2.23042	4.29840	2.22700	4.45948	0.15	−3.61
1.62	2.31752	4.41307	2.31731	4.57193	0.01	−3.47
1.64	2.40693	4.52966	2.40989	4.68650	−0.12	−3.35
1.66	2.49869	4.64820	2.50478	4.80296	−0.24	−3.22
1.68	2.59285	4.76874	2.60202	4.92140	1.35	−3.10

only by 0.073% in that interval. We conclude that a lower limit of about 0.5 K for the liquid branch of Eq. (1) is a conservative estimate, and that a lower limit of 0.2 K may be acceptable if the predicted small negative expansivity below 0.48 K can be ignored in any particular application.

Down to 0.48 K, the maximum deviation of the rectilinear density $(\rho_L + \rho_V)/2$ from the critical density is 0.28%. At 1.62 K, the deviation is only 0.053%. To our knowledge, such a small deviation over a wide temperature range has not been previously observed for any other fluid.

8. CONCLUSION

A review of data for the saturated- vapor and liquid densities of ^{3}He is made in this paper, and a density equation is presented. The mathematical form of the equation is asymptotically correct at the critical point. The average relative error of predicted values against the experimental values is 0.39%. There are only 16 points out of 205 with relative errors above 1%. The equation joins smoothly to the ^{3}He second virial equation at about 1.62 K. On the liquid side, the equation appears valid down to at least 0.48 K, while the calculated liquid density remains acceptably accurate down to 0.2 K. The rectilinear density deviates from the critical density by less than 0.28% down to 0.48 K. This equation can not only be used to calculate the saturated density of ^{3}He, but also can be of great significance in building the equation of state for ^{3}He in both the gas and liquid regions.

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