A density equation for saturated helium-3*

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An accuracy satisfying density equation of saturated vapor and liquid ^{3}He is obtained by nonlinear regression based on experimental data collected after a thorough survey of literatures. This equation not only can be used to calculate saturated density of ^{3}He independently, but also is to be of great significance in building the equation of state for ^{3}He in both gas and liquid regions. For a better understanding of the equation, the saturated density curves of ^{3}He and ^{4}He are compared.

INTRODUCTION

^{3}He is one of the two stable isotopes of helium in nature. Because of its unique physical properties, ^{3}He has many important applications in various fields. Almost all the applications of ^{3}He involves its thermodynamic properties, therefore scientists and engineers need a convenient, comprehensive, and accurate database for ^{3}He properties in their design and research. From the mid 20th century, studies on properties of ^{3}He have been carried out with intense interests, however, the problem is that the experimental data were scattered in literatures from 1950s until now, and there is no reported work of systematic collection of experimental data and equations covering full regions of gas, liquid and solid. A project on establishing a database for thermodynamic and transport properties of gaseous and normal liquid ^{3}He, is being carried out in Cryogenics Laboratory, Zhejiang University. Although saturated vapor pressure equation was published in 1964, which was used to define the 1962 temperature scale, no accurate saturated density equation in a wide range has been presented. This paper is to introduce the work of collecting experimental data and building the density equation of saturated vapor and liquid ^{3}He, an important step of the whole project. This equation not only can be used to calculate saturated density of ^{3}He and act as a boundary to identify the gas and liquid phase of ^{3}He, but also will be a significant reference for ^{3}He equation in both gas and liquid regions and provide the initials for properties calculation.

^{3}He PHASE DIAGRAM

The atomic weight of ^{3}He is 3.016; the atomic nucleus is made up of 2 protons and 1 neutron; ^{3}He is a colorless, odorless, innoxious, and nonflammable inert gas under normal conditions. Under normal pressures, ^{3}He gas can only be liquefied until the temperature reaches below 3.191K, and it is impossible

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to obtain solid ^{3}He at atmospheric pressure at any temperature including the absolute zero. Like liquid ^{4}He, liquid ^{3}He doesn't have a triple point and can exist in either of 2 very different states --- the normal liquid and the superfluid liquid; the λ-transition temperature is 2.6mK. The phase diagram of ^{3}He is shown in Figure1 while the characteristic points on the diagram are shown in Table 1. (The dot line on the diagram separates the regions with positive and negative thermal expansion coefficient α.)

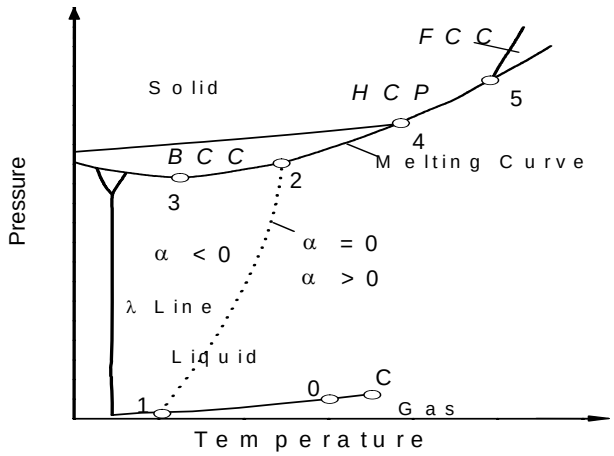

Figure 1 ^{3}He P-T Phase Diagram

Table 1 Characteristic Points Data on ^{3}He Phase Diagram [1]

Characteristic Points	T (K)	P (Mpa)
C (Critical point)	3.324	0.1165
λ Line	0.0026	
0 (Normal boiling point)	3.191	0.101325
1 ($\alpha=0$)	0.502	0.2736×10^{-4}
2 ($\alpha=0$)	1.26	4.7623
3 ($P=P_{min}$)	0.32	2.9303
4 (^{3}He Liquid-BCC-HCP equilibrium)	3.138	13.7234
5 (^{3}He Liquid-FCC-HCP equilibrium)	17.78	162.93

Table 2 Density or Specific Volume of Saturated Vapor and Liquid ^{3}He

Source of Data	Temp. Range	Phase and Number
Grilly et al. (1949) [2]	1K-3.34K	Liquid & Vapor (14)
Kerr (1954) [3]	1K-3.3K	Liquid & Vapor (28)
Пешков (1957) [4]	1.4K-3.29K	Liquid & Vapor (12)
Sherman & Edeskuty (1960)[5]	0.8K-3K	Liquid (23)
Kerr & Taylor (1962) [6]	0.2K-3.2K	Liquid (57)
Sherman (1965) [7]	2.4K-3.324K	Liquid & Vapor (28)
Wallace & Meyer (1970) [8]	3.0K-3.310K	Liquid & Vapor (34)
Chase & Zimmerman (1973) [9]	3.2K-3.309K	Liquid & Vapor (43)

DENSITY DATA OF SATURATED ^{3}He

Experimental density data of ^{3}He on the saturated curve are shown in Table 2. Before nonlinear regression we made a preliminary filter to the collected 239 points of experimental data. Considering that the data by Grilly et al. [2] were made relatively earlier when the measuring technique was relatively unreliable and the understanding of ^{3}He properties was just on the horizon, and their data seem to deviate away from other data, it is decided not to use their data. In addition, some data near the critical point with great deviation were also eliminated. After filtering, 205 points of experimental data were left.

DENSITY EQUATION OF SATURATED ^{3}He

After comparison, the nondimensional form of density equation was determined and can be expressed as (the only difference between liquid and vapor branches is the sign before the middle terms):

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

where $\tau = (T_c - T)/T_c$, T_c is the critical temperature, ρ_c is the critical density, $c_1 \sim c_6$ are the constant coefficients obtained by least squares regression, and β is a critical index to describe the density dependence near critical point. As the fitting result is very sensitive to the critical parameters, it is then very important to determine the values of these parameters. After careful comparison, we decide to use critical parameters by Chase and Zimmerman [9]: T_c = 3.3093K, ρ_c = 41.191Kg/m^3, *and* β = 0.3653. The results of regression are shown in Table 3 and Table 4.

Table 3 Technical Results of Regression

Number of observations	205
Convergence tolerance factor	1.00000000E-10
Number of iterations performed	7
Final sum of squared deviations	4.1179188E-3
Final sum of deviations	2.2542236E-1
Standard error of estimate	0.00454896
Average deviation	0.1727264
Maximum deviation for any observation	1.040135
Average relative deviation	0.360%
Maximum relative deviation	1.995%
Number of points with relative deviation larger than 2%	0
Number of points with relative deviation larger than 1%	16
Proportion of variance explained (R^2)	1.0000 (100.00%)
Adjusted coefficient of multiple determination (Ra^2)	1.0000 (100.00%)
Durbin-Watson test for auto-correlation	0.535

Table 4 Calculated Coefficient Values

Coefficient	Value	Standard dev.
c_1	1.34598418	0.002580188
c_2	-0.0738744808	0.02311163
c_3	-0.506778465	0.05545185
c_4	0.225069671	0.03864127
c_5	0.00700440506	0.004916735
c_6	-0.0104634733	0.007278005

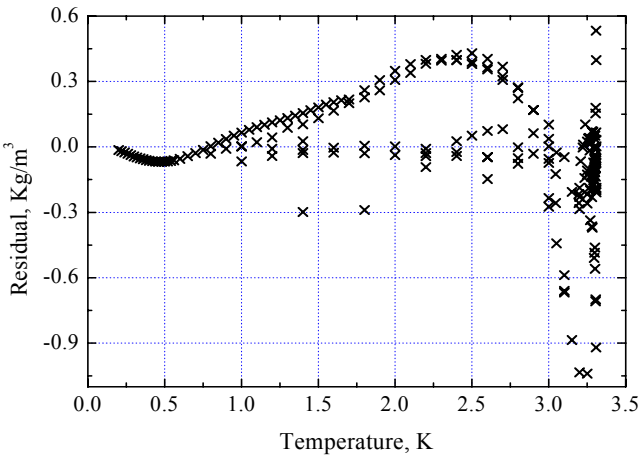

Figure 2 Residual ($\rho_{cal} - \rho_{exp}$) Distribution

By comparing the calculated values obtained by Equation (1) with the experimental data, it is found that the relative error of any observation is within 2%, and the average relative error of all data is 0.360%. There are only 16 points with relative error larger than 1%, in which the maximum is 1.995%. Most of these 16 points are in the critical region close to critical point, because the properties of ^{3}He in this region are very complicated so that the measurement becomes difficult to be accurate. The distribution of absolute residual is shown in Figure 2.

Figure 3 shows all the 239 experimental data of saturated vapor and liquid ^{3}He and the curve generated by Equation (1) of this work. It indicates that this equation can represent the property of ^{3}He density on saturated curve accurately.

SATURATED DENSITY COMPARISON BETWEEN ^{3}He AND ^{4}He

Figure 4 shows the comparison of saturated density curves of ^{3}He and ^{4}He. From the diagram, it is noted that the most significant differences of the two curves are the different critical points which lead to different normal boiling points, different temperature and density ranges. It is also noted that there is an interesting similarity between the two saturated curves so it is then possible to make a scaling from ^{4}He

which is relatively known to ^{3}He. This is also a possible work for us in the future.

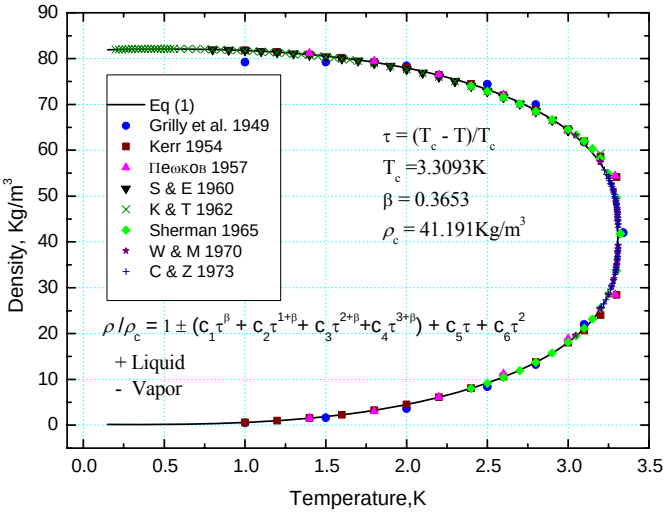

Figure 3 ^{3}He Saturated Density Curve

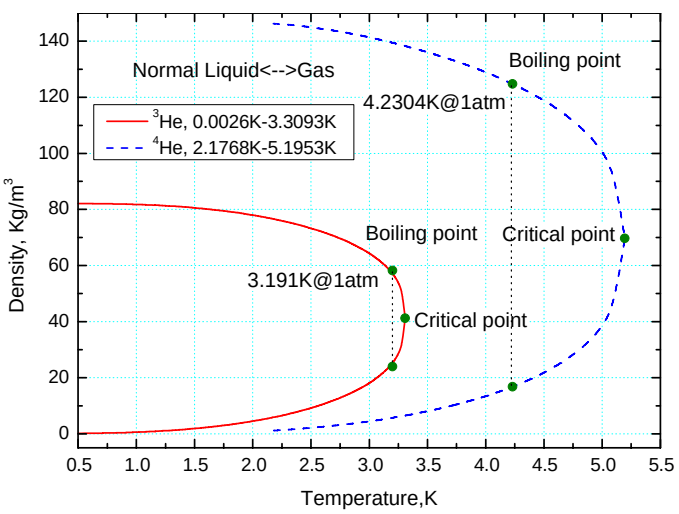

Figure 4 Saturated Density Curves of ^{3}He and ^{4}He

CONCLUSION

The present work made a collection of density data of saturated vapor and liquid ^{3}He, and obtained an accuracy satisfying density equation. The average relative error of calculated values from experimental values is 0.360%, while the maximum relative error is 1.995%. There are only 16 points out of 205 with the relative error above 1%. This equation not only can be used to calculate saturated density of ^{3}He independently, but also is to be of great significance in building the equation of state for ^{3}He in both gas and liquid regions. The similarity of saturated density curves of ^{3}He and ^{4}He suggests a possibility of scaling.

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