Int J Thermophys (2010) 31:774–783
DOI 10.1007/s10765-009-0695-y

Thermodynamic Diagrams of ^{3}He from 0.2 K to 300 K Based Upon its Debye Fluid Equation of State

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Received: 25 June 2009 / Accepted: 15 December 2009 / Published online: 5 January 2010

Abstract On the basis of the equation of state and the phase equilibrium equations of helium-3 (^{3}He), a computer program for calculating the thermodynamic properties of ^{3}He has been created. With this program, many iso-property tables were prepared for generating *p*–*h* and *T*–*s* diagrams of ^{3}He over the range of temperature from 0.2 K to 300 K and pressures up to 300 MPa. Compared with the previous diagrams plotted with interpolated experimental data sets, the new ones are more thermodynamically consistent and cover a broader temperature and pressure range. The estimated overall random errors of the diagrams are within 2 %.

Keywords Helium-3 · *p*–*h* diagram · *T*–*s* diagram

1 Introduction

Thermodynamic diagrams are useful for scientists and engineers to understand the thermodynamic states and phase transitions of a fluid and the consequences of using this fluid. They have lines, a bit confusing at first, showing the "solutions" to a set of equations. That is, they give a quick way to determine the actual (observational) behavior (how one thermodynamic property changes with the other, such as temperature). Temperature–entropy (*T*–*s*) and pressure–enthalpy (*p*–*h*) are typical diagrams widely used in the thermodynamics community. Such diagrams are available for most

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of the pure fluids common in industry, such as oxygen, nitrogen, and helium-4, over wide temperature and pressure ranges. For helium-3, however, only very limited studies are available. In 1970, Daunt [1] plotted the first simple *T*–*s* chart with isobars and isenthalps for temperatures up to 10 K and pressures up to 3 MPa. He realized some serious inconsistencies existed between the *s*–*T* and *h*–*T* data in the temperature range from 1 K to 20 K, especially at the lower temperatures. This represents only a first approximation to the thermodynamic data for ^{3}He, and it was difficult to assess the accuracy of the data, and moreover, interpolation of the data either between isobars or between isenthalps was also very difficult. Kraus et al. [2] experimentally obtained the isotherms in a *p*–*h* diagram of ^{3}He in the range $1.0\,\mathrm{K} \leq T \leq 4.17\,\mathrm{K}$ and $0 \leq p \leq 0.65\,\mathrm{MPa}$ by means of the isothermal throttle effect. It was claimed that the diagram was determined with an error of 5 %. Most recently, Huang et al. [3] released more comprehensive versions of both *T*–*s* and *p*–*h* diagrams in the range of temperature from 1 K to 20 K and pressures up to 20 MPa, which was restricted by the fact that there are no experimental data found above 20 K and no equation of state was available at that time. However, many applications, such as cryocooler design, require larger scale plots. Therefore, this article extends the scope of *T*–*s* and *p*–*h* diagrams for ^{3}He and provides more thermodynamically consistent data from 0.2 K to 300 K and pressures up to 300 MPa. Instead of using only mathematical interpolation/extrapolation to smoothed *p*–*ρ*–*T* data, the equation of state for ^{3}He and the vapor–liquid and liquid–solid equilibrium ancillary equations were used as data sources.

2 Data Preparation and Diagram Plotting

p–*h* and *T*–*s* diagrams usually show a net of five different lines: (1) isobars, lines of constant pressure; (2) isotherms, lines of constant temperature; (3) isochores, lines of constant specific volume; (4) isentropes, lines of constant entropy; and (5) isenthalps, lines representing constant enthalpy. Hence, before starting to dot the diagram plotting, the bulk *p*–*ρ*–*T*, entropy, and enthalpy property data should be prepared. As mentioned above, the data source for the *T*–*s* and *p*–*h* diagrams for ^{3}He in this article includes calculations by a set of equations of state. The dominant equation of state adopted was proposed by Huang et al. [4] in 2006, which was derived from a Debye specific-heat model based on classical thermodynamics and quantum mechanics. This general equation of state, implicit in the Helmholtz energy as a function of temperature and density, works well both for the compressed liquid and gaseous ^{3}He, including the supercritical area. It covers the temperature range from the ^{3}He superfluid transition temperature, 2.6 mK, to 500 K (and could be extended to 1500 K), and pressures up to 300 MPa. Ancillary phase equilibrium equations for ^{3}He with high precision are also necessary for plotting the diagrams, which are namely, the vapor pressure equation [5], the saturated density equation [6], the melting pressure equation, and the melting density equation [7]. The equations along the liquid–vapor equilibrium line work at temperatures from 2.6 mK to the critical point, 3.3157 K, while the ones along the liquid–solid equilibrium line hold good from 2.6 mK to 30 K. One state parameter, *T* or *p*, is enough for calculations of the saturation properties and the melting properties, while a pair of input parameters is needed for the normal compressed region.

The pressure, enthalpy, and entropy could be derived from the Helmholtz-implicit equation of state through the following thermodynamic relations,

$$p = \rho^2 \frac{\partial A}{\partial \rho}, \tag{1}$$

$$h = A - T\frac{\partial A}{\partial T} + \rho \frac{\partial A}{\partial \rho}, \tag{2}$$

$$s = -\frac{\partial A}{\partial T}, \tag{3}$$

where A is the Helmholtz energy, T is the temperature, and ρ is the density.

A Fortran program was compiled to calculate all the properties in the range of temperature from 0.2 K to 300 K, and pressures up to 300 MPa. It provides several modes for iso-property calculations, which output the target data tables directly. Combining all the tables, the *p*–*h* and *T*–*s* plots for ^{3}He could be generated, as shown in Figs. 1, 2, 3, and 4. For the *p*–*h* diagram, a logarithmic scale is used for the pressure, but a linear scale is used for the entropy, due to the amplitude of the numerical variation. In a similar manner, both temperature T and entropy s use a linear scale on the *T*–*s* diagram.

3 Accuracy Analyses

The accuracy of the *p*–*h* and *T*–*s* plots are, in fact, dominated by the equation of state and the effective figure control during the iteration. The tolerance $\varepsilon = 10^{-6}$ is taken as the interaction accuracy. Given temperature and density, the uncertainty for the pressure, specific heat, and sound speed calculated by the Debye state equation are generally within 1 % [6] in the range of temperature from 0.01 K to 300 K and pressure from 0 MPa to 300 MPa. The average relative error for the vapor-pressure equation and the saturation-density equation are 0.2 % [3] and 0.28 % [4], respectively, from 0.0026 K to 3.3157 K. The average relative error for the melting pressure equation is 0.22 % [5] from 0.001 K to 35 K, while the ones for the melting density equation on the liquid side and solid side are 0.24 % and 0.22 % [5], respectively. The overall uncertainties for *p*–*ρ*–*T*, enthalpy, and entropy of the *p*–*h* and *T*–*s* diagrams are estimated to be within 2 %.

Comparisons between the calculations in this article with previous studies will help to evaluate the performance of the diagrams presented here. Table 1 lists the entropy calculations of ^{3}He along the saturated liquid and vapor lines, which are also shown in Fig. 5. It can be seen that the calculations agree well with each other, except those from Singwi [8], which were taken in the earliest year and diverged from the others at the lower temperatures. The solid line was calculated by using the Debye equation of state together with the phase equilibrium ancillary equations introduced in the above text. It is a good fit to scattered data over a narrow temperature range and hence describes the entropy of ^{3}He on the saturation line.

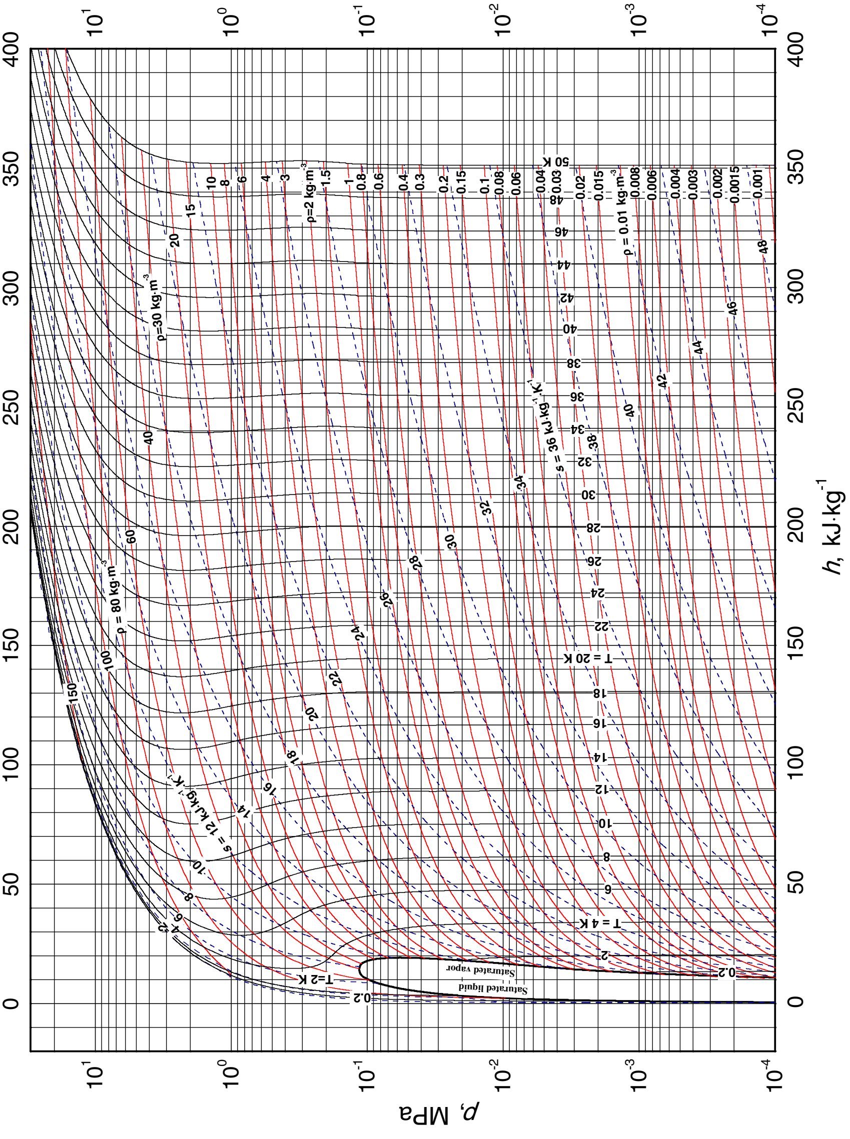

Fig. 1 *p–h* diagram of helium-3 (0.2 K to 50 K)

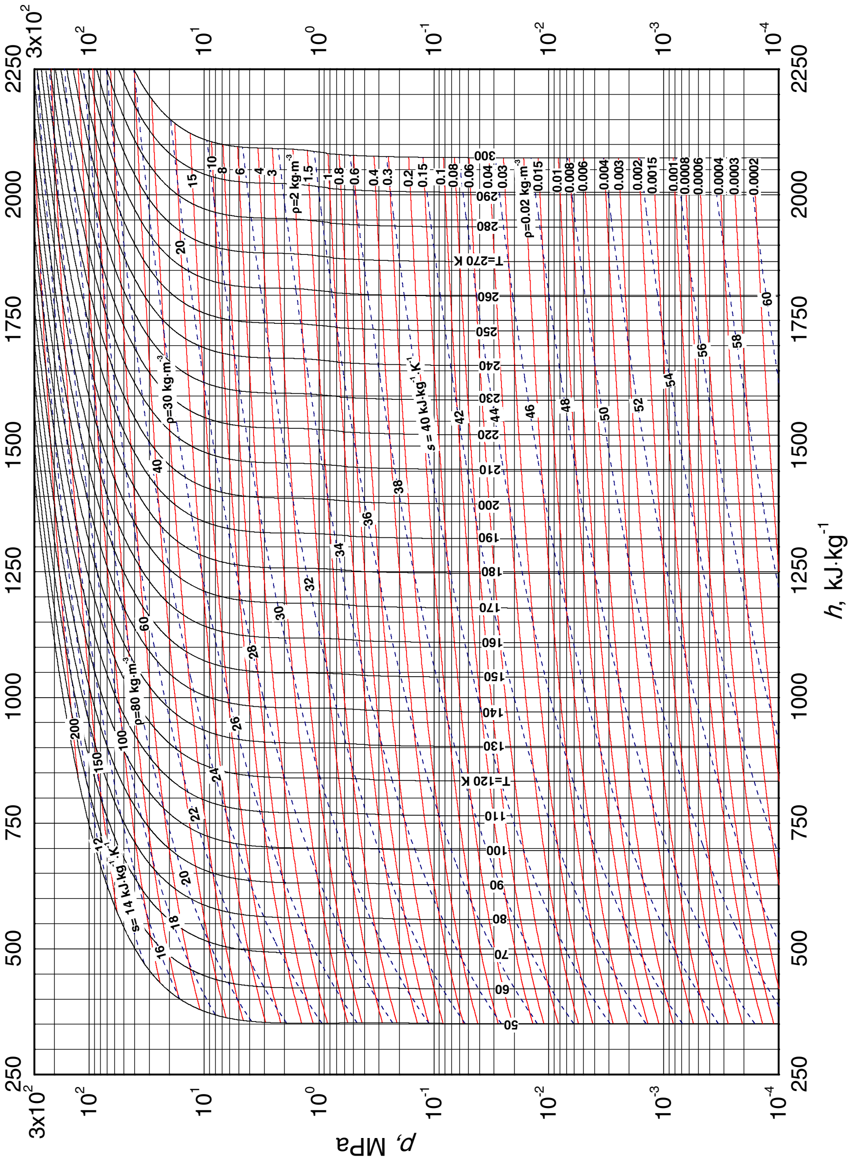

Fig. 2 *p*–*h* diagram of helium-3 (50 K to 300 K)

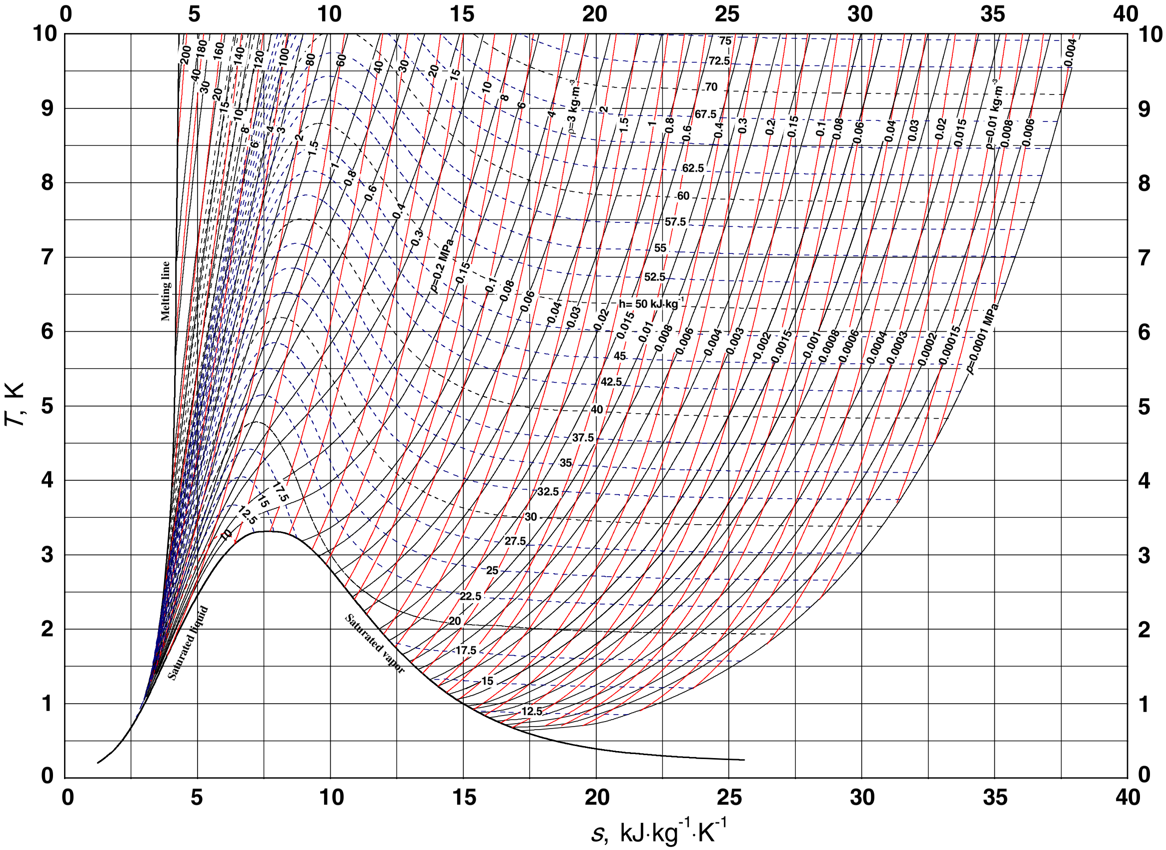

Fig. 3 *T*–*s* diagram of helium-3 (0.2 K to 10 K)

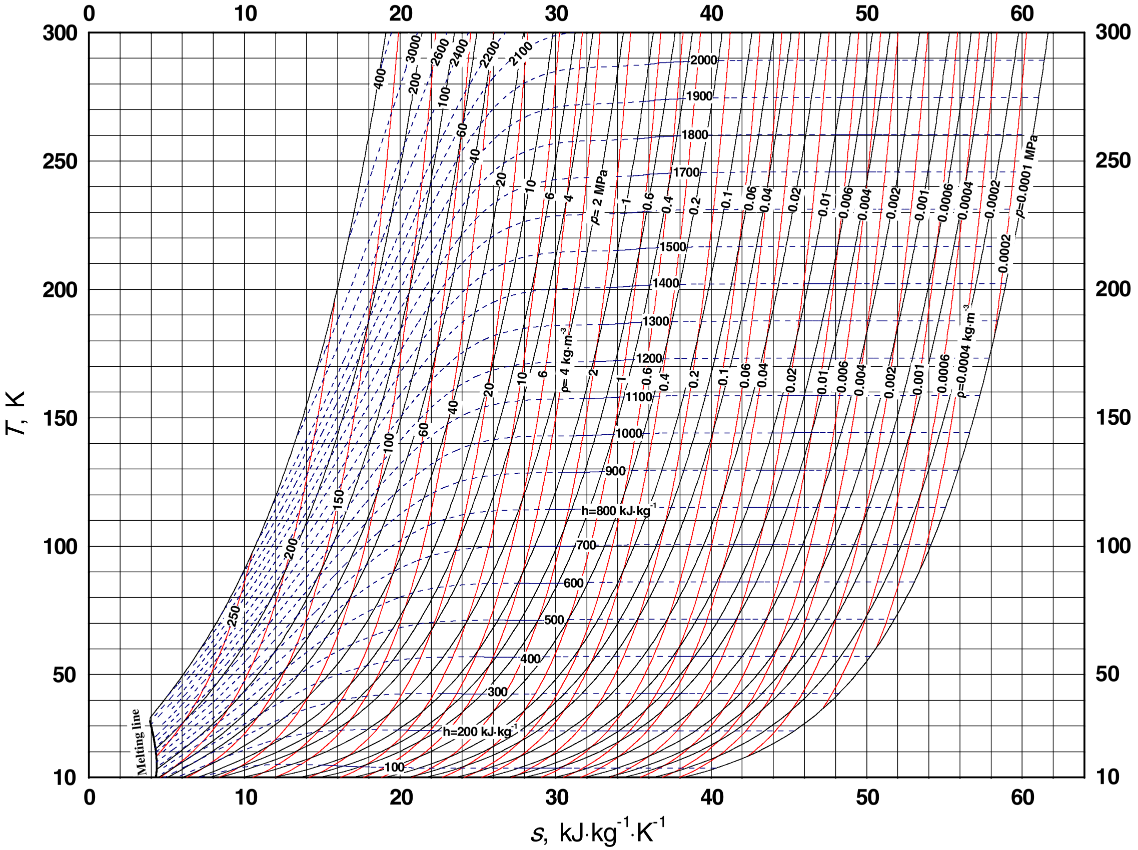

Fig. 4 T–s diagram of helium-3 (10 K to 300 K)

Table 1 Data sources of entropy of saturated ^{3}He

Year	Authors	Number of points	T range (K)
1952	Singwi [8]	10	0.24–2.96
1955	Roberts and Sydoriak [9]	14	0.4–2.5
1955	Abraham et al. [10]	16	0.2384–1.9735
1959	Brewer et al. [11]	13	0.15–0.75
1959	Brewer and Daunt [12]	15	0.12–1
1961	Strongin et al. [13]	7	0.1–0.23
1961	Lee et al. [14]	9	0.2–1
1961	Rauch [15]	26	0.1–2
1964	Roberts et al. [16]	10	0.2–2
1966	Colyer [17]	11	0.2025–2.4937

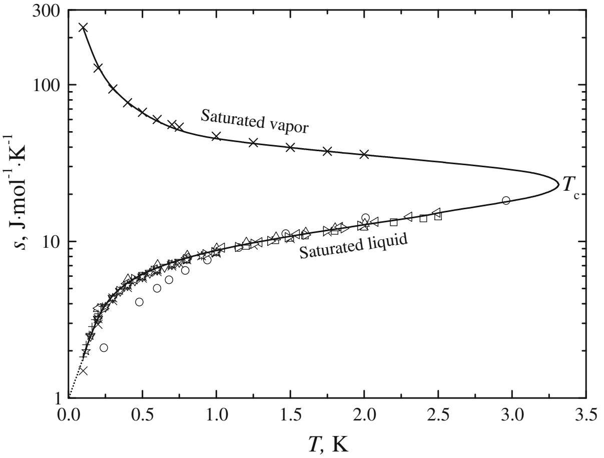

Fig. 5 Entropy of saturated helium-3; ○—Singwi [8]; □—Roberts and Sydoriak [9]; ▹—Abraham et al. [10]; ▽—Brewer et al. [11]; ☆—Brewer and Daunt [12]; +—Strongin et al. [13]; ∗—Lee et al. [14]; ×—Rauch [15]; △—Roberts et al. [16]; ◃—Colyer [17]; Solid line—calculations on the saturated liquid

Table 2, together with Fig. 6, presents the studies of the enthalpies on the saturated line of ^{3}He. The reference point for zero enthalpy of Rauch's data [15] is the saturated vapor at 0 K, which means the enthalpy for the saturated liquid is negative. In order to keep all the data consistent, in Fig. 6, Rauch's data have been shifted with

Table 2 Data sources of enthalpy of saturated ^{3}He

Year	Authors	Number of points	T range (K)
1961	Rauch [15]	28	0–2
1966	Colyer [17]	15	0.1472–2.434
1976	Betts [18]	34	0.2–1

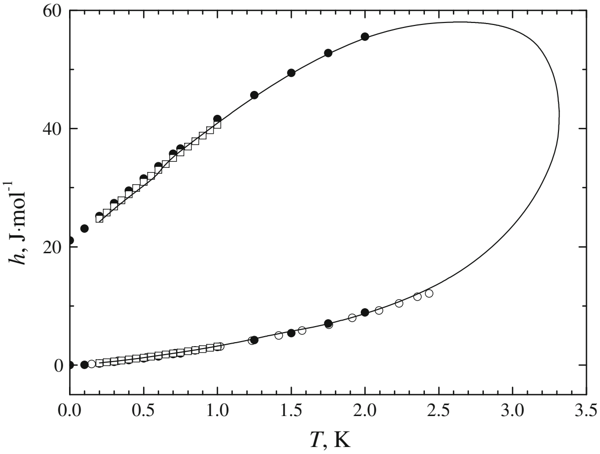

Fig. 6 Saturated enthalpy of helium-3; ●—Rauch [15]; ○—Colyer [17]; □—Betts [18]; Solid line—calculations on the saturated liquid

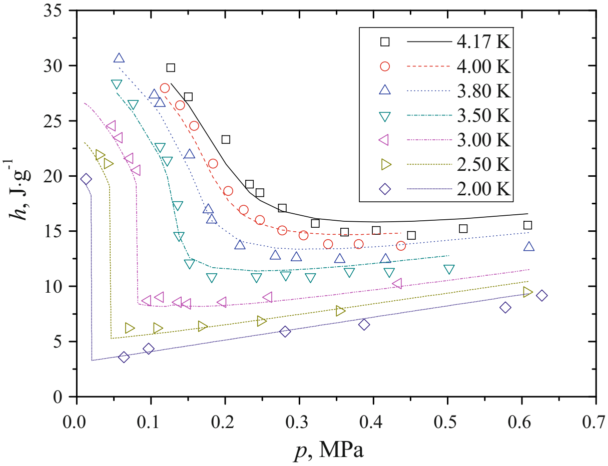

Fig. 7 Isotherm comparisons between Kraus' plot and the one in this article

a value of 21.08736 $\text{J} \cdot \text{mol}^{-1}$, which is equal to the latent heat of evaporation of ^{3}He at 0 K. After shifting, Rauch's data agree well with the others, which are all very well fitted by the solid line representing the smooth calculations by the equation of state.

Here, we also check the agreement between Kraus' simple plots [2] and ours. Obviously different reference values for enthalpy are used. By making shifts exactly like the one introduced above for the saturated enthalpy, the lines in Figs. 7 and 8 from the new *p*–*h* diagram for isotherms and isobars agree with those of Kraus quite well and gives even better performance.

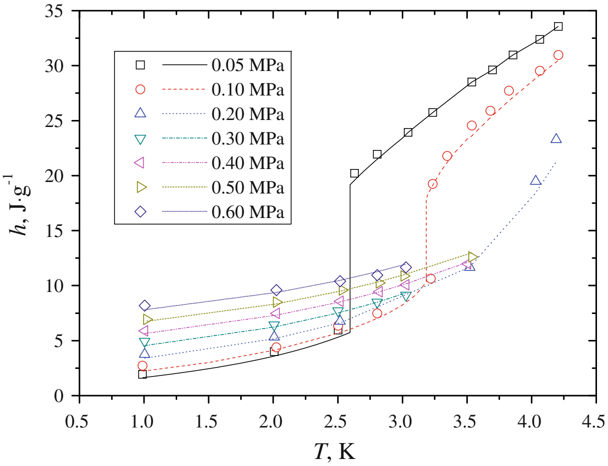

Fig. 8 Isobar comparisons between Kraus' plot and the one in this article

Conclusion

p–h and T–s diagrams for (^{3}He) over a wide range of temperature from 0.2 K to 300 K and pressures up to 300 MPa were plotted based on the equation of state, saturation equation, and melting equation for ^{3}He. The uncertainties of the p–h and T–s diagrams are generally within 2 %, which satisfies the requirement of engineering applications.

Acknowledgments This study is supported by National Natural Science Foundation of China (Grant No. 50806047), and Doctoral Fund of Ministry of Education of China (Grant No. 200802481108).

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