Discussion on Gibbons' equation of state for helium-3*

Huang Y.H., Chen G.B., Li X.Y.

Cryogenics Laboratory, Zhejiang University, Hangzhou 310027, P.R. China

A thorough literature survey was made to obtain all useful information relating to helium-3. Based on this fundamental work, the Gibbons' equation of state for ^3He in the gaseous region from 4K to 20K at pressures 0.1MPa to 10MPa was tested and refitted, and a modified form was presented.

INTRODUCTION

Helium-3, as the most expensive rare gas, is being gradually applied in the realm of high-tech and fundamental science. Many scientists have showed their interests in the thermodynamic and transport properties of ^3He.Although most of the experimental and theoretical research work on ^3He had already been done since the middle of the last century, many valuable experimental reference data and theoretical models were scattered among various literatures. Due to lack of a comprehensive, united database for the thermodynamic and transport properties of ^3He, a project on these properties of normal liquid and gaseous ^3He has been carried out in Cryogenics Laboratory, Zhejiang University. A thorough literature survey was made to obtain all existing data relating to ^3He for the following properties: PVT data, equilibrium data, melting point, critical point, latent heat, specific heat, entropy, expansion coefficients, compression coefficients, velocity of sound, thermal conductivity and viscosity. Based on this fundamental work, the Gibbons' equation of state (EOS) [1] for ^3He in the region from 4K to 20K at pressures 0.1MPa to 10MPa was tested and refitted, and a modified form was presented.

COLLECTION OF EXPERIMENTAL DATA

Firstly, all available literatures on ^3He since 1949 which contain useful information were classified and indexed by the authors for convenience. Then valuable data, figures and correlations or EOSs were inputted into computer as computer-readable documents. This work concerns the information of the saturated vapor and liquid, the normal liquid region, the gas region, the melting curve and the critical region etc of ^3He. Here for examples, Figures 1 and 2 show the 3D distribution of PVT in 0.2K-3K and specific heat, respectively.

GIBBONS' EQUATION OF STATE FOR GASEOUS ^3He

In 1967, Gibbons and Nathan brought forward an EOS of ^3He (See Equation (1)) for the gas region from

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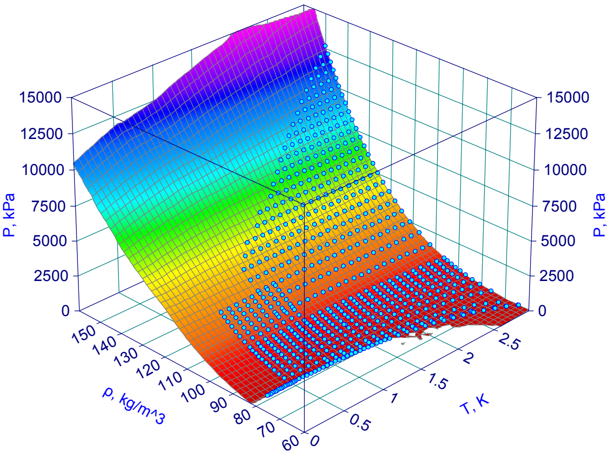


Figure 1 PVT distribution of ^{3}He

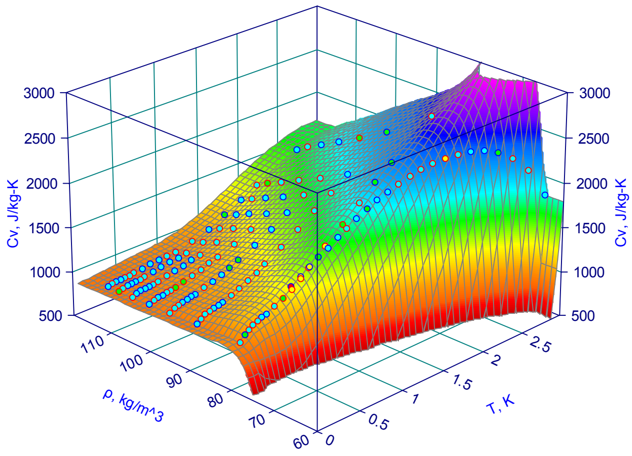


Figure 2 Specific heat distribution of ^{3}He

4K to 20K at pressures 0.1 to 10MPa. The corresponding coefficients are listed in Table 1 after a least square fitting to 336 experimental data points. Gibbons said that the maximum error in the pressure was 2.5% and the average error was 0.7% [1].

$$T(Z-1)=(N_1+\frac{N_2}{X}+\frac{N_3}{X^2}+\frac{N_4}{X^3})\rho+(N_5T+N_6+\frac{N_7}{X})\rho^2+N_8\rho^3+N_9\rho^4+N_{10}\rho^5 \\ +\left[(\frac{N_{11}}{X^2}+\frac{N_{12}}{X^3}+\frac{N_{13}}{X^4})\rho^2+(\frac{N_{14}}{X^2}+\frac{N_{15}}{X^3})\rho^4\right]\exp(-\frac{N_{16}}{T}) \tag{1}$$

where $X=T+5.6906$, ρ is density in mol/l and $Z=P/\rho RT$ is the compressibility factor. P is pressure in atm. If we use SI unit MPa for pressure, $Z=9.8692\cdot P/\rho RT$.

Table 1 The initial coefficients of Gibbons' equation

N_1 = 0.711661079×10^{-1}	N_5= -0.103027537×10^{-4}	N_9 = 0.111831781×10^{-8}	N_{13}= -0.467828934×10^{2}
N_2 = -0.264145152×10^{1}	N_6 = 0.123947764×10^{-2}	N_{10} = 0.63176889 ×10^{-8}	N_{14} =-0.89772816 ×10^{-4}
N_3 = 0.205080136×10^{2}	N_7= -0.641439718×10^{-2}	N_{11} = -0.203977574	N_{15}= 0.470376428×10^{-3}
N_4 = -0.32981763 ×10^{3}	N_8 = 0.158411494×10^{-5}	N_{12} = 0.668353927×10^{1}	N_{16} = 0.73596×10^{-2}

We compare the pressure predicted by Equation (1) with the coefficients given in Table 1 and the collected experimental data, which partly used by Gibbons et al themselves. Unfortunately, the results indicated that the equation can not express the experimental data distribution accurately. It has a maximum error 182.03% and an average error 27.27%. There are 498 points out of total 600 data records with an error greater than 5%. The authors firstly thought that some literal errors might be occurred, but we found that the equation and coefficients in other literatures [2, 3] turn out to be the same as Equation (1) and Table (1).

MODIFICATIONS TO EQUATION (1)

Refitting Equation (1)

First, the basic form of Gibbons' equation (1) is still used to make a nonlinear regression with those experimental data we collected. Then we refitted the coefficients, given in Table 2, and compared the predicted values and the experimental observations. It is found that only 16 points out of total 600 experimental records have a relative error greater than 5% and 45 points greater than 3%. The maximum and average errors are 14.18% and 1.194%, respectively. Obviously, the statistical results are much better than those generated by Equation (1) with the original coefficients.

Table 2 Refitted coefficients for equation (1)

N_1 = 6.17194320552383E-1	N_5 = 4.32113547815425E-4	N_9 = -2.91237878499204E-5	N_{13} =9.72104073531524E+0
N_2 = -1.91531493414952E+1	N_6 = -2.22439026331829E-2	N_{10} =3.56069188211502E-7	N_{14} = -1.94416104080400E-4
N_3 =1.23487003861953E+2	N_7 = 1.84867792880005E-1	N_{11} =-4.22210226133859E-1	N_{15} =1.97960175514069E-3
N_4 = -1.35913310975649E+3	N_8 = 1.09489564515292E-3	N_{12} = 1.14520483939277E+0	N_{16} = -5.67114133250345E+0

Modifying Equation (1)

On the basis of the above work and plenty of empirical trial, we obtained a modified form of Gibbons' equation, which can express the PVT surface of gaseous ^{3}He in the temperature region 4K-20K very well, see Equation (2). The coefficients are listed in Table 3.

$$\begin{aligned} T(Z-1) = &\{N_1 + N_2 T + \frac{N_3}{T+N_0} + \frac{N_4}{(T+N_0)^2} + \frac{N_5}{(T+N_0)^3} + \frac{N_6}{(T+N_0)^4}\}\rho + (N_7 T + N_8 + \frac{N_9}{T+N_0})\rho^2 \\ &+\{N_{10}T + N_{11} + \frac{N_{12}}{T+N_0} + \frac{N_{13}}{(T+N_0)^2} + \frac{N_{14}}{(T+N_0)^3} + \frac{N_{15}}{(T+N_0)^4}\}\rho^3 + (N_{16}T + N_{17} + \frac{N_{18}}{T+N_0})\rho^4 + N_{19}\rho^5 \\ &+\{[\frac{N_{20}}{(T+N_0)^2} + \frac{N_{21}}{(T+N_0)^3} + \frac{N_{22}}{(T+N_0)^4}]\rho^2 + [\frac{N_{23}}{(T+N_0)^2} + \frac{N_{24}}{(T+N_0)^3} + \frac{N_{25}}{(T+N_0)^4}]\rho^4\}\exp(-\frac{N_{26}}{T}) \end{aligned} \tag{2}$$

Table 3 Coefficients for Equation (2)

N_0= 1.37913054616371E+01	N_9 = -1.78125335499170E+01	N_{18}= -5.66286520059774E-03
N_1= -8.47271117750707E+00	N_{10}= 2.18996380714379E-04	N_{19}= 4.32113723739915E-07
N_2= 1.68593794065112E-01	N_{11}= 8.01717914362068E-04	N_{20}= -9.18876483522023E+02
N_3= 5.62665344888040E+00	N_{12}= -1.38065195665170E+00	N_{21}= 1.90660089948584E+04
N_4= 1.35205917030388E+04	N_{13}= 7.82901309576907E+01	N_{22}= -1.24336066467970E+05
N_5= -3.40048252460412E+05	N_{14}= -1.53157150932023E+03	N_{23}= -3.19768785811710E-01
N_6= 2.51846515212280E+06	N_{15}= 1.02688572589399E+04	N_{24}= 6.89110717561145E+00
N_7= -1.63437319145173E-02	N_{16}= -4.93385536008283E-06	N_{25}= -4.85698353122027E+01
N_8= 1.07275069012551E+00	N_{17}= 3.08888230842748E-04	N_{26}= 1.20249749298560E+01

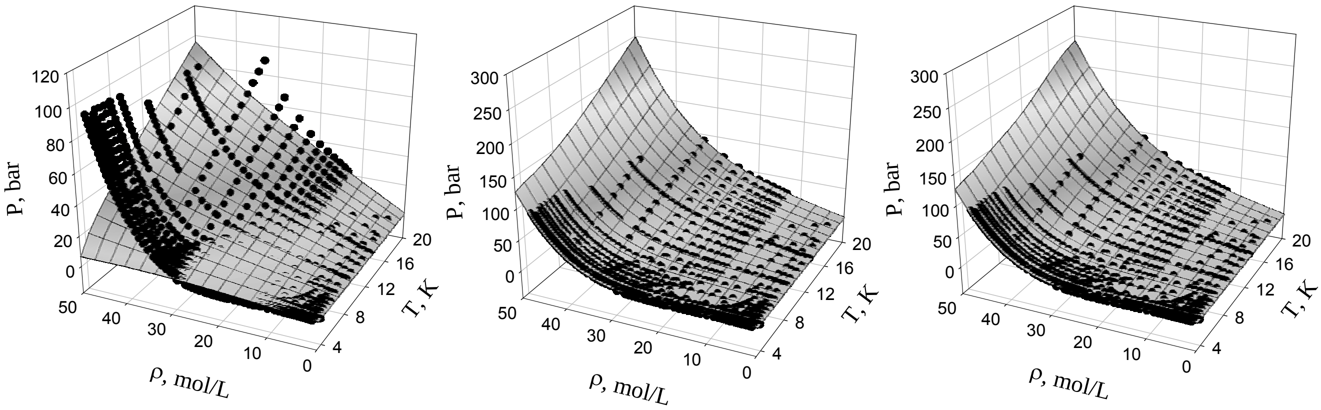
The maximum and average error of pressures predicted by Equation (2) with the coefficients listed in Table 3 is 9.94% and 1.11676%, respectively. There are only 10 points out of total 600 data records with an error greater than 5% and 40 points greater than 3%. So, this model is much better than Equation (1).

RESULTS AND ANALYSIS

To compare the performance of the equations mentioned above clearly, Table 4 and Figure 5 give their parameters and surface distribution. We can see that the refitted Gibbons' equation improved the agreement with the experimental observations obviously. And the accuracy can be further improved by using Equation (2) but with more coefficients. Further study showed that although the refitted Equation (1) and Equation (2) can express the PVT surface very well, their first and second derivative properties such as the specific heat could not be derived from both of them accurately. Hence, a new structure EOS is needed to describe all the thermodynamic parameters uniformly.

Table 4 Contrast of the three equations (Total 600 experimental data records)

Statistical Parameters	Original Gibbons' equation	Refitted Gibbons' Equation	Equation (2)
Average error	27.27%	1.194%	1.117%
Max error	182.03%	14.18%	9.94%
Number of points >5%	498	16	10
Number of points >3%	531	45	40



(a) Original Gibbons' equation (b) Refitted Gibbons' Equation (c) Equation (2)

Figure 5 Contrast of the surface generated by the three equations

CONCLUSIONS

The refitted Gibbons' equation can express the PVT properties of ^{3}He much better than the initial one in the gaseous region from 4K to 20K at pressures up to 10MPa. Then a modified form of the equation of state was brought forward with the average and maximum relative error 1.117% and 9.94% respectively. This equation can be used to predict the PVT properties of low temperature gaseous ^{3}He for technical application and to be a good reference to future study.

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