Critical Properties of Isobaric Processes of Lennard-Jones Gases

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The thermodynamic quantities of Lennard-Jones gases, evaluated till the fourth virial coefficient, are investigated for an isobaric process. A partition function in the T-P grand canonical ensemble $Y(T,P,N)$ may be defined by the Laplace transform of the partition function $Z(T,V,N)$ in the canonical ensemble. The Gibbs free energy is related with $Y(T,P,N)$ by the Legendre transformation $G(T,P,N) = -kT\log Y(T,P,N)$. The volume, enthalpy, entropy, and heat capacity are analytically expressed as functions of the intensive variables temperature and pressure. Some critical thermodynamic quantities for Xe are calculated and drawn. At the critical point the heat capacity diverges to infinity, while the Gibbs free energy, volume, enthalpy, and entropy are continuous. This suggests that a second-order phase transition may occur at the critical point.

Key words: Lennard-Jones Gases; Isobaric Process; Critical Constants;
Second-order Phase Transition.

1. Introduction

Recently, the critical properties of van der Waals gases at isobaric processes have been investigated [1]. Their thermodynamic functions are presented as analytical expressions of the intensive variables temperature and pressure. The heat capacity, thermal expansivity and isothermal compressibility consequently diverge to infinity at the critical point. The volume, entropy and enthalpy are continuous at the critical point, whereas these quantities show a sudden change in the neighbourhood of the critical point. These behaviours of thermodynamic quantities correspond to the second kind of phase transition at the critical point [1, 2]. Up to now, the virial equation of state and some thermodynamic quantities for imperfect gases [3] have been derived from the Helmholtz free energy, using the partition function $Z(T,V,N)$ of a canonical ensemble in classical statistical mechanics. Any singularity of the thermodynamic quantities in a canonical ensemble may not be found even if N or V approaches infinity.

On the other hand, the Takahasi nearest-neighbour gas [4 – 7] has been introduced as the simplest model within one-dimensional imperfect gases in classical statistical mechanics over 60 years ago. The partition function $Y(T,P,N)$ in the T-P grand canonical ensemble [5 – 7] may be defined by the Laplace transform of the partition function $Z(T,V,N)$ in a canonical ensemble in classical statistical mechanics,

$$Y(T,P,N) = \int_0^\infty Z(T,V,N)\exp\left(-\frac{PV}{RT}\right)\mathrm{d}V. \quad (1)$$

The partition function reaches the Gibbs free energy by the Legendre transformation

$$G(T,P,N) = -kT\ln Y(T,P,N). \quad (2)$$

The Gibbs free energy is consequently replaced by a function of the two intensive variables T and P. From the viewpoint of an isobaric process, this may be significant to provide the properties of thermodynamic quantities for the second-order phase transition for Lennard-Jones gases in the neighbourhood of the critical point $(T_\mathrm{c}, P_\mathrm{c}, V_\mathrm{c})$. The third and fourth virial coefficients for the Lennard-Jones (12-6) potential have been evaluated through numerical integrations by Kihara [8], Hirschfelder *et al.* [9], and Barker and Monaghan [10], respectively.

In this work, the expansion coefficients for the fourth virial coefficient are calculated by using the results of numerical integrations [11]. The Gibbs free energy is analytically expressed by the two intensive variables temperature and pressure. The volume, enthalpy, entropy and heat capacity are included as variables. These thermodynamic quantities are determined by numerical calculations and are graphically displayed for an isobaric process. The second-order phase transition of Lennard-Jones gases at the critical point is discussed.

2. Thermodynamic Quantities of Lennard-Jones Gases at Isobaric Processes

The partition function for imperfect gases in classical statistical mechanics [3, 9] is represented by

$$Z(T,V,N) = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \cdot \exp\left[N\left(1+\ln V - \frac{B}{V} - \frac{C}{2V^2} - \frac{D}{3V^3}\right)\right], \quad (3)$$

where B, C and D are the second, third and fourth virial coefficients, respectively. By using the Laplace transform of $Z(T,V,N)$ the partition function in the T-P grand ensemble can be written in the form

$$Y(T,P,N) = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \cdot \int_0^\infty \exp\left[N\left(1+\ln V - \frac{B}{V} - \frac{C}{2V^2} - \frac{D}{3V^3} - \frac{PV}{RT}\right)\right] \mathrm{d}V. \quad (4)$$

If N becomes very large, one can replace the integral by the maximum value of the integrand, as is done in statistical mechanics. This is called the saddle point method. If the derivative of the integrand in (4) equals zero, we can obtain the quartic equation for V, which is equivalent to the virial equation of state till the fourth virial coefficient:

$$V^4 - \frac{RT}{P}V^3 - \frac{RTB}{P}V^2 - \frac{RTC}{P}V - \frac{RTD}{P} = 0. \quad (5)$$

According to (2) and the integral of (4), the Gibbs free energy per mol is expressed as

$$G(T,P) = -RT\left[A + 1 + \frac{3}{2}\ln T + \ln V - \frac{B}{V} - \frac{C}{2V^2} - \frac{D}{3V^3}\right] + PV, \quad (6)$$

A is written as

$$A = \frac{3}{2}\ln\frac{2\pi mk}{h^2} = 46.6826 + \ln M, \quad (7)$$

where M is the molecular weight. V in (6), given by a root of the quartic equation (5), is represented as a function of the intensive variables T and P. We can exactly solve the quartic equation for V in (5). Substituting $V = x + RT/4P$, the standard cubic equation without x^3 can be replaced by

$$x^4 + ax^2 + bx + c = 0. \quad (8)$$

The coefficients a, b and c are given as

$$a = -6\left(\frac{RT}{4P}\right)^2 - \frac{RTB}{P}, \quad (9)$$

$$b = -8\left(\frac{RT}{4P}\right)^3 - \frac{(RT)^2B}{2P^2} - \frac{RTC}{P}, \quad (10)$$

and

$$c = -3\left(\frac{RT}{4P}\right)^4 - \frac{(RT)^3B}{16P^3} - \frac{(RT)^2C}{4P^2} - \frac{RTD}{P}. \quad (11)$$

Equation (8) is resolved into two real factors of the second degree [12]: that is

$$\left(x^2 + \sqrt{z}x + p\right)\left(x^2 - \sqrt{z}x + q\right) = 0. \quad (12)$$

If we compare this product with the proposed equation, we find an equation for z

$$z^3 + 2az^2 + (a^2 - 4c)z - b^2 = 0. \quad (13)$$

The cubic equation in (13) is called the resolvent cubic equation for the quartic equation. Substituting $z = y + a_0$, the standard cubic equation, missing y^2, can be replaced by

$$y^3 + 3Py - 2Q = 0. \quad (14)$$

The coefficients a_0, P and Q result from

$$a_0 = -\frac{2}{3}a, \quad (15)$$

$$P = -\left(a_0^2 - \frac{a^2}{3} + \frac{4c}{3}\right), \quad (16)$$

and

$$Q = a_0^3 - \frac{a_0}{2}(a^2 - 4c) + \frac{b^2}{2}. \quad (17)$$

The determinant for the cubic equation in (13) is defined as

$$D = P^3 + Q^2. \quad (18)$$

If $P > P_\mathrm{c}$, the determinant is always positive, and a real root and two complex conjugated roots are given. Especially, if the determinant is zero, there is a triple real root that is called the critical volume, V_c. This condition corresponds to the critical state $(T_\mathrm{c}, P_\mathrm{c}, V_\mathrm{c})$. This point, $(P_\mathrm{c}, V_\mathrm{c})$ is found to be the inflection point in the P-V curve at the critical temperature. A real root within $D > 0$ is given by

$$z = -\frac{2a}{3} + \sqrt[3]{R_1} + \sqrt[3]{R_2} \tag{19}$$

with

$$R_1 = Q + \sqrt{D} \tag{20}$$

and

$$R_2 = Q - \sqrt{D}. \tag{21}$$

Applying z in (19) to the quartic equation in (12), a suitable root is obtained:

$$\begin{aligned} V &= \frac{RT}{4P} + \frac{1}{2}\left(-\sqrt{z} + \sqrt{U_1}\right), \\ U_1 &= -z - 2a + \frac{2b}{\sqrt{z}}, \end{aligned} \tag{22}$$

or

$$\begin{aligned} V &= \frac{RT}{4P} + \frac{1}{2}\left(\sqrt{z} + \sqrt{U_2}\right), \\ U_2 &= -z - 2a - \frac{2b}{\sqrt{z}}. \end{aligned} \tag{23}$$

All thermodynamic quantities can be derived from the Gibbs free energy in the known way. Since the coefficient in the term $(\mathrm{d}V/\mathrm{d}T)_P$ satisfies the virial equation of state in (5), the volume is given as the form missing $(\mathrm{d}V/\mathrm{d}T)_P$,

$$V = \left(\frac{\partial G}{\partial P}\right)_T = V. \tag{24}$$

V is equal to the positive root in (22) or (23). The entropy is obtained as

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_P \\ &= R\Big[A + \frac{5}{2} + \frac{3}{2}\ln T + \ln V - \frac{B}{V} - \frac{C}{2V^2} \\ &\quad - \frac{D}{3V^3} - T\Big(\frac{1}{V}\frac{\mathrm{d}B}{\mathrm{d}T} + \frac{1}{2V^2}\frac{\mathrm{d}C}{\mathrm{d}T} + \frac{1}{3V^3}\frac{\mathrm{d}D}{\mathrm{d}T}\Big)\Big]. \end{aligned} \tag{25}$$

The enthalpy is obtained as

$$\begin{aligned} H &= -T^2\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_P \\ &= RT\left[\frac{3}{2} - T\left(\frac{1}{V}\frac{\mathrm{d}B}{\mathrm{d}T} + \frac{1}{2V^2}\frac{\mathrm{d}C}{\mathrm{d}T} + \frac{1}{3V^3}\frac{\mathrm{d}D}{\mathrm{d}T}\right)\right] \\ &\quad + PV. \end{aligned} \tag{26}$$

The heat capacity at constant pressure is easily derived from the enthalpy:

$$\begin{aligned} C_P &= \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_P \\ &= R\Big[\frac{3}{2} - 2T\Big(\frac{1}{V}\frac{\mathrm{d}B}{\mathrm{d}T} + \frac{1}{2V^2}\frac{\mathrm{d}C}{\mathrm{d}T} + \frac{1}{3V^3}\frac{\mathrm{d}D}{\mathrm{d}T}\Big) \\ &\qquad + T^2\Big(\frac{1}{V^2}\frac{\mathrm{d}B}{\mathrm{d}T} + \frac{1}{V^3}\frac{\mathrm{d}C}{\mathrm{d}T} + \frac{1}{V^4}\frac{\mathrm{d}D}{\mathrm{d}T}\Big)\frac{\mathrm{d}V}{\mathrm{d}T} \\ &\qquad - T^2\Big(\frac{1}{V}\frac{\mathrm{d}^2B}{\mathrm{d}T^2} + \frac{1}{2V^2}\frac{\mathrm{d}^2C}{\mathrm{d}T^2} + \frac{1}{3V^3}\frac{\mathrm{d}^2D}{\mathrm{d}T^2}\Big)\Big] \\ &\quad + P\frac{\mathrm{d}V}{\mathrm{d}T}, \end{aligned} \tag{27}$$

where the derivative of V containing U_1 with respect to T can be given as

$$\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{R}{4P} + \frac{1}{4}\left(-\frac{1}{\sqrt{z}}\frac{\mathrm{d}z}{\mathrm{d}T} + \frac{1}{\sqrt{U_1}}\frac{\mathrm{d}U_1}{\mathrm{d}T}\right). \tag{28}$$

The derivative of U_1 with respect to T can be written in the form

$$\frac{\mathrm{d}U_1}{\mathrm{d}T} = -2\frac{\mathrm{d}a}{\mathrm{d}T} + \frac{2}{\sqrt{z}}\frac{\mathrm{d}b}{\mathrm{d}T} - \left(1 + \frac{b}{2\sqrt{z^3}}\right)\frac{\mathrm{d}z}{\mathrm{d}T} \tag{29}$$

with

$$\begin{aligned} \frac{\mathrm{d}z}{\mathrm{d}T} &= -\frac{2}{3}\frac{\mathrm{d}a}{\mathrm{d}T} + \frac{1}{3{R_1}^{2/3}}\left(\frac{\mathrm{d}Q}{\mathrm{d}T} + \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}T}\right) \\ &\quad + \frac{1}{3{R_2}^{2/3}}\left(\frac{\mathrm{d}Q}{\mathrm{d}T} - \frac{1}{2\sqrt{D}}\frac{\mathrm{d}D}{\mathrm{d}T}\right), \end{aligned} \tag{30}$$

and $\mathrm{d}a/\mathrm{d}T$, $\mathrm{d}b/\mathrm{d}T$, $\mathrm{d}Q/\mathrm{d}T$ and $\mathrm{d}D/\mathrm{d}T$ can easily be obtained. Also the derivative of V containing U_2 can easily be done.

The Lennard-Jones (12,6) potential

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma^6}{r}\right)\right] \tag{31}$$

Table 1. Expansion coefficients for the third and fourth virial coefficients for the Lennard-Jones (12-6) potential.

j	$c^{(j)}$	$c^{(j)}$ [9]	$d^{(j)}$	j	$c^{(j)}$
0	1.73006E+0	+1.729	0.300013	18	−1.44996E-3
1	−3.18534E+0	−3.203	5.140382	19	−7.21048E-4
2	1.51458E+0	+1.519	−25.656539	20	−3.50522E-4
3	9.52881E-1	+0.958	39.248691	21	−1.66821E-4
4	4.26919E-1	+0.429	−16.943306	22	−7.78255E-5
5	5.75415E-2	+0.059	−2.299947	23	−3.56288E-5
6	−1.42042E-1	−0.140		24	−1.60215E-5
7	−2.12681E-1	−0.210		25	−7.08257E-6
8	−2.07342E-1	−0.205		26	−3.08025E-6
9	−1.68490E-1	−0.168		27	−1.31880E-6
10	−1.22584E-1	−0.123		28	−5.56189E-7
11	−8.24356E-2	−0.084		29	−2.31182E-7
12	−5.21638E-2	−0.059		30	−9.47508E-8
13	−3.14070E-2	−0.035			
14	−1.81307E-2	−0.020			
15	−1.00906E-2	−0.011			
16	−5.43694E-3	−0.006			
17	−2.84527E-3	−0.004			

has been used for the calculation of the virial coefficients. We shall use the symbols B^*, C^* and D^* to denote B/b_0, $C/{b_0}^2$ and $D/{b_0}^3$, where $b_0 = 2/3N\pi\sigma^3$ and σ is the length parameter in (31). B^* and C^* [8,9] have been represented as

$$B^* = \sum_{j=0}^{\infty} b^{(j)} T^{*-(3+6j)/12}; \qquad b^{(j)} = \frac{2^{j+1/2}}{4j}\Gamma\left(\frac{2j-1}{4}\right) \tag{32}$$

and

$$C^* = \sum_{j=0}^{\infty} c^{(j)} T^{*-(j+1)/2}, \tag{33}$$

where $T^* = kT/\varepsilon$. The $b^{(j)}$ are the expansion coefficients, which are written as an analytic formula and have numerically been calculated [9]. The $c^{(j)}$ are the expansion coefficients, which are calculated again by numerical integrations, as shown in Table 1. Assuming that D^* is expressed as

$$D^* = \sum_{j=0}^{5} d^{(j)} T^{*-(3/4+j)}, \tag{34}$$

the $d^{(j)}$ are expansion coefficients which are optimized for 11 points in the region from 1.1 to 1.7 for T^* using data of D^* [11] and are shown in Table 1.

These coefficients in the series expansion are generally applicable to all gases that consist of the characteristic parameters ε and σ for the Lennard-Jones (12-6) potential. The first and second derivatives of B^*, C^* and D^* are easily obtained as analytic functions to T.

Table 2. Parameters for the Lennard-Jones (12-6) potential determined from experimental data of the second virial coefficients [13].

Gas	ε/kT	σ/Å	Gas	ε/kT	σ/Å
Ne	35.086	2.737	Ar	118.63	3.445
Kr	164.89	3.669	Xe	224.80	4.053
N2	95.040	3.669	O2	119.37	3.454
CO	100.17	3.760	CH_4	149.07	3.798
C_2H_4	209.33	4.329	C_2H_6	232.06	4.395

Comparing thermodynamic functions of imperfect gases with those of ideal gases, we may introduce the partition function $Y(T,P,N)$ applying the Laplace transform of the semi-classical partition function for ideal gases $Z(T,V,N)$ [3] for V:

$$\begin{aligned} Y(T,P,N) &= \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \frac{1}{N!} \\ &\quad \cdot \int_0^{\infty} V^N \exp\left(-\frac{PV}{RT}\right) \mathrm{d}V \\ &= \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \left(\frac{RT}{P}\right)^{N+1}. \end{aligned} \tag{35}$$

The Gibbs free energy is expressed as

$$G = -RT\left(A + \ln R - \ln P + \frac{5}{2}\ln T\right), \tag{36}$$

where A is equivalent to A in (7). The entropy is obtained as

$$S = R\left(A + \frac{5}{2} + \ln R - \ln P + \frac{5}{2}\ln T\right). \tag{37}$$

Successively, the volume V, enthalpy H and heat capacity C_P are equal to RT/P, $5/2RT$ and $5/2R$, respectively.

3. Numerical Results

In the above-mentioned cases, most thermodynamic functions, are written as functions of the intensive variables T and P. The parameters ε and σ for the Lennard-Jones (12-6) potential for 10 gases are determined from the experimental data of second virial coefficients [13] by the least squares method as shown in Table 2. The critical constants, T_c, P_c and V_c are derived from the condition that the determinant of the resolvent cubic equation in (13) is zero at which there

Table 3. Critical constants for the critical temperature (T_c/K), critical pressure (P_c/atm) and critical volume (V_c/cm^{3}mol^{-1}).

	This work			Experimental result [14]		
Gas	T_c	P_c	V_c	T_c	P_c	V_c
Ne	45.4	28.2	41.8	44.4	27.2	41.7
Ar	153.7	48.0	81.5	150.8	48.1	74.9
Kr	213.6	55.2	97.7	209.4	54.3	91.2
Xe	291.3	55.9	133.6	289.7	57.6	118
N2	123.2	31.9	101.9	126.2	33.5	89.5
O2	154.7	47.9	83.5	154.6	49.8	73.4
CO	129.8	31.1	108.8	132.9	34.5	93.1
CH_4	193.1	45.0	107.5	190.6	45.4	99.0
C_2H_4	271.2	42.7	162.0	282.4	49.7	129
C_2H_6	300.7	45.2	171.3	305.4	48.2	148

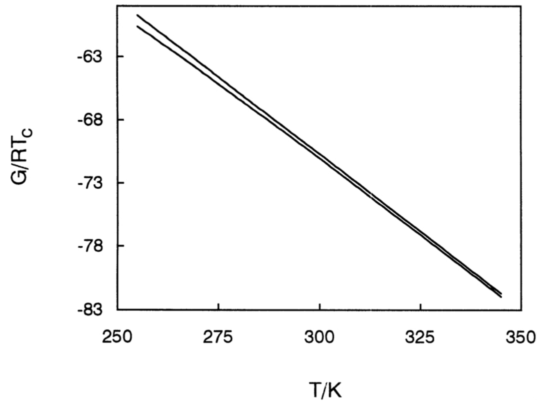

Fig. 1. The Gibbs free energy of Xe (lower curve), plotted against the temperature at $P_c = 55.9$ atm. The upper curve is due to the ideal gas. $T_c = 291.3$ K.

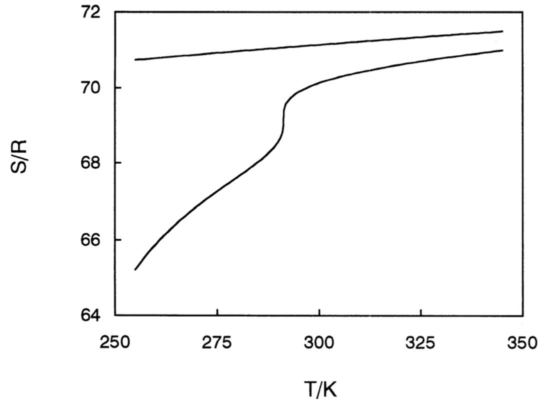

Fig. 2. The entropy of Xe (lower curve), plotted against the temperature at $P_c = 55.9$ atm. The upper curve is due to the ideal gas. $T_c = 291.3$ K.

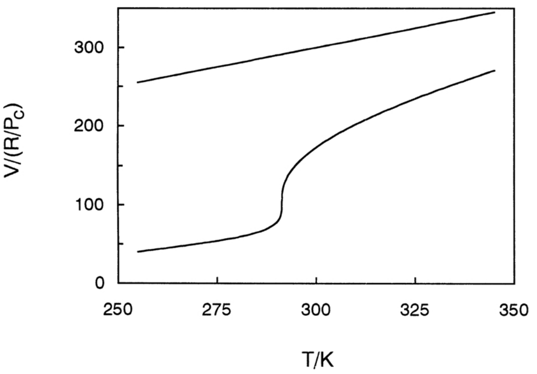

Fig. 3. The volume of Xe (lower curve), plotted against the temperature at $P_c = 55.9$ atm. The upper straight line is obeyed by the Gay-Lussac law. $T_c = 291.3$ K.

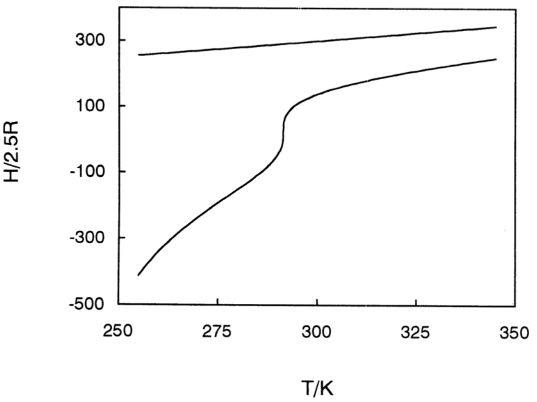

Fig. 4. The enthalpy of Xe (lower curve), plotted against the temperature at $P_c = 55.9$ atm. The upper straight line is due to the ideal gas. $T_c = 291.3$ K.

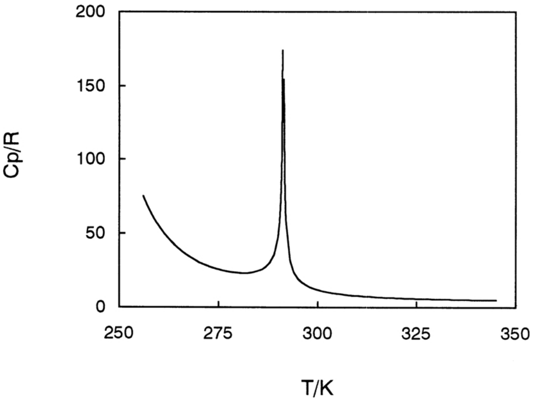

Fig. 5. The heat capacity at constant pressure of Xe, plotted against the temperature at $P_c = 55.9$ atm. $T_c = 291.3$ K.

are triple roots. Although the virial equation of state is approximated till the fourth virial coefficient, the critical temperatures and pressures in Table 3 may be qualitatively evaluated, while the critical volumes for all gases except Ne are deviated from experimental results [14]. Numerical results obtained with these thermodynamic functions for Xe at $P_c = 55.9$ atm are displayed in Figures 1 – 5. The Gibbs free energy consists of two slightly different tangents on both sides at $T_c = 291.3$ K, while else it formed continuous curve. The volume, entropy and enthalpy are continuous at $T_c = 291.3$ K, whereas these quantities show a sudden change in the neighbourhood of the critical point. The heat capacity at $P_c = 55.9$ atm diverges to infinity at $T = 291.3$ K. As shown in Figs. 1 – 5, the thermodynamic quantities at $T > 291.3$ K approach asymptotically those of ideal gases. Comparing with van der Waals gases [1], the reliability of shapes for the heat capacity at $T \ll T_c$ may be doubtful because the virial equation of state is too roughly approximated till the fourth virial coefficient only. A singularity of the heat capacity, however, is found at the critical point. This singularity suggests a phase transition. The generalized diagrams of some thermodynamic quantities accompanying a second-order phase transition are typically described in textbooks of physical chemistry [2]. Comparing Figs. 1 – 5 with these diagrams [2], the behaviour in the neighbourhood of the critical point corresponds to a second-order phase transition.

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