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Equation of State for Substances that Satisfy the Corresponding States Law

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Universal expressions for the free energy of substances that satisfy the law of corresponding states are obtained. The equation of state is constructed using an interpolation between the high temperature Debye approximation and the ideal-gas one. Missing data needed for calculations have been found from the comparison of calculated and tabulated values of entropy and pressure along the phase coexistence curves. The thermodynamics of corresponding states, constructed in this way, allows one to find the triple- and critical-point parameters, as well as the phase coexistence curves with an accuracy that does not exceed the accuracy of the law of corresponding states itself.

KEY WORDS: corresponding state law; critical point; equation of state; triple point.

1. INTRODUCTION

It is known [1–3] that the class of substances that satisfy the law of corresponding states includes the gas and condensed phases of such substances as rare gases, N_2, O_2, CO, CH_4, and fullerenes. All of the thermodynamic parameters of these substances expressed in dimensionless form coincide closely. It is also important that there is a rich body of experimental information on the thermodynamic properties of this group of materials. This information is available in thermophysical property handbooks [4, 5]. However, the lack of a unified analytical description of the thermodynamics for this group of substances causes certain difficulties, for example, in hydrodynamic calculations and other applications. The existing empirical and semi-empirical equations of state are valid in a limited domain of the phase diagram.

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In this paper, we show that the basis of the construction of corresponding states thermodynamics can be sought in the expression for the free energy, obtained in the high temperature limit of the Debye theory. The equation of state ensuing from this theory and expressed in reduced molecular dimensionless units does not depend on a specific substance. On the basis of this expression, we built interpolation formulae for the free energy of solid and liquid states expanded from the limit of high temperatures and low densities as ideal-gas states. In these equations, we take into account the peculiarities of the liquid state which is connected with a high value of its configurational entropy. The free energy constructed in this way contains two unknown functions: the dependence of the Debye temperature on volume and the potential components of the free energy. The first one is found from the condition that the entropy constructed on the basis of our model must correspond to tabulated data for this thermodynamic function along the coexistence curves of different phases. It is shown that this function is universal for all substances that satisfy the law of corresponding states and can be approximated by a simple formula. "Cold" (i.e., temperature-independent) components of pressure are found as the differences between the expressions for pressure, following from the interpolation formula, and the pressure along the coexistence curves taken from the thermophysical properties handbooks [4, 5]. The cold curves constructed in this way in dimensionless units are also universal for all of the substances of the chosen group.

Thus, we construct an analytical expression for the free energy of corresponding states describing the solid, liquid, and gas phases. Calculations of the triple- and critical-point parameters and coexistence curves according to our equation of state are in good agreement with tabulated data.

2. CORRESPONDING STATES IN REDUCED UNITS

Reduced units are composed from the different combinations of the three basic units: D is the depth of the intermolecular potential, σ is the "diameter" corresponding to the distance at which the potential is equal to zero, and m is the mass of an atom. So the "molecular" unit of distance is σ, temperature is D, density is m/σ^3, and pressure is D/σ^3. The corresponding reduced units for pressure p, density ρ, and temperature T are expressed as

$$p^* = p\sigma^3/D; \quad \rho^* = \rho\sigma^3/m; \quad T^* = T/D \tag{1}$$

The parameters of the interaction potential for two noble gas atoms can be found from an analysis of physical properties, which depend on this potential. For solidified and liquefied noble gases, these parameters could be determined from the differential and full scattering cross section, the second virial coefficient, the diffusion coefficient, the thermal conductivity, the viscosity, and the excitation spectrum for diatomic molecules of noble gases. Reliable interaction potentials for two noble gas atoms have been constructed [6–9] from measurements and processing of these quantities. The resulting parameters $r_{\min} = 2^{1/6}\sigma$ and D for Ne, Ar, Kr, and Xe are given in Table I taken largely from Ref. 3. The parameters at the critical and triple points in dimensional and dimensionless units are also presented in Table I.

Values of the Debye temperature T_D are also given in Table I. This temperature characterizes the vibrational energy in the condensed states. From the basic molecular units, it is possible to form a quantity with dimensions of frequency, $\sqrt{D/m}/\sigma$. The temperature corresponding to the vibrational energy with this frequency is $T_{D0} = h\sqrt{D/m}/\sigma k$ where k is the Boltzmann constant. The relationship T_D/T_{D0} is close to a constant value. This means that the concept of corresponding state can be applied to this value too.

Table I. Parameters of the Pair Interaction Potential for Rare-Gas Atoms and the Base Reduced Thermodynamic Parameters [3][a]

Gas parameter	Ne	Ar	Kr	Xe
$r_{\min} = 2^{1/6}\sigma$ (Å)	3.09	3.76	4.01	4.36
D (meV)	3.64	12.3	17.3	24.4
D (K)	42	143	200	278
μ (g·mol^{-1})	20.18	39.95	83.8	131.3
$p_0 = D/\sigma^3$ (atm)	286	525	608	666
$\rho_0 = m/\sigma^3$ (g·cm^{-3})	1.61	1.76	3.05	3.72
T_c (K)	44.4 (1.05)	150.9 (1.06)	209.4 (1.04)	289.7 (1.02)
p_c (atm)	27.6 (0.097)	49 (0.093)	55 (0.0905)	58.4 (0.087)
ρ_c (g·cm^{-3})	0.484 (0.30)	0.535 (0.304)	0.919 (0.301)	1.11 (0.298)
T_{tr} (K)	24.55 (0.584)	83.78 (0.586)	115.76 (0.579)	161.36 (0.58)
p_{tr} (atm)	0.433 (0.0013)	0.687 (0.0013)	0.73 (0.0013)	0.816 (0.0013)
v_l (cm^3·g^{-1})	0.801 (1.28)	0.707 (1.25)	0.409 (1.25)	0.337 (1.25)
v_s (cm^3·g^{-1})	0.70 (1.12)	0.618 (1.09)	0.358 (1.09)	0.301 (1.12)
v_g (cm^3·g^{-1})	226.6 (363)	243.4 (430)	152.9 (466)	121.9 (453)
T_D (K)	75	92	72	64
T_{D0} (K)	22.9	24.63	18.85	16.33
T_D/T_{D0}	3.28	3.73	3.82	3.92
B	0.217	0.069	0.038	0.024

[a] Values in parenthesis are given in reduced units.

The plots of (a) the pressure and (b) the phase equilibrium densities versus temperature along the phase coexistence curves are presented in Fig. 1. Curves 1 to 4 correspond to the solidification curve, melting curve, vaporization curve, and condensation curve, respectively. The values [4, 5] are denoted by symbols. For these plots, we use thermodynamic functions for noble gases [4, 5] that are consistent with the entire body of experimental data on thermal properties of noble gases. We can see that the law of corresponding states with some error is valid for all coexistence curves. The exception is the sublimation curve. Deviations from the law of corresponding states occur along the latter at low temperatures. We do not consider properties of this domain of the phase diagram.

3. FREE ENERGY IN REDUCED UNITS

Let us write the well-known expressions for the free energy of an ideal gas and of a solid in the high temperature limit of the Debye theory using reduced units. The ideal gas free energy has the form,

$$F(v,T)=\frac{RT}{\mu}\left(\ln\frac{\Lambda^3}{eg_a mv}\right), \tag{2}$$

where g_a is the inner statistical sum of an atom, v is the specific volume, $\Lambda=h/\sqrt{2\pi mT}$ is the thermal wavelength, and e is the base of the natural logarithm. Let us write the expression for the dimensionless free energy $F^*=F\mu/RD$, introducing the reduced units. We obtain

$$F^*=3T^*\ln\left(\frac{B}{ev^{*1/3}\sqrt{T^*}}\right) \tag{3}$$

In Eq. (3)

$$B=h/\sigma\sqrt{2\pi mD} \tag{4}$$

is the de Boer parameter. The values of this parameter, characterizing quantum corrections to thermodynamic functions, are given in Table I. A smaller value of this parameter corresponds to smaller corrections. Neon has the largest value of this parameter for the systems considered. Therefore, its thermodynamic functions deviate to the greatest degree from common rare gas dependences (see Fig. 1). From here on, the asterisks and the multiplier g_a (of no practical significance) will be omitted. From Eq. (3), it follows that the dependence on class of substance appears as the value 3 $\ln B$.

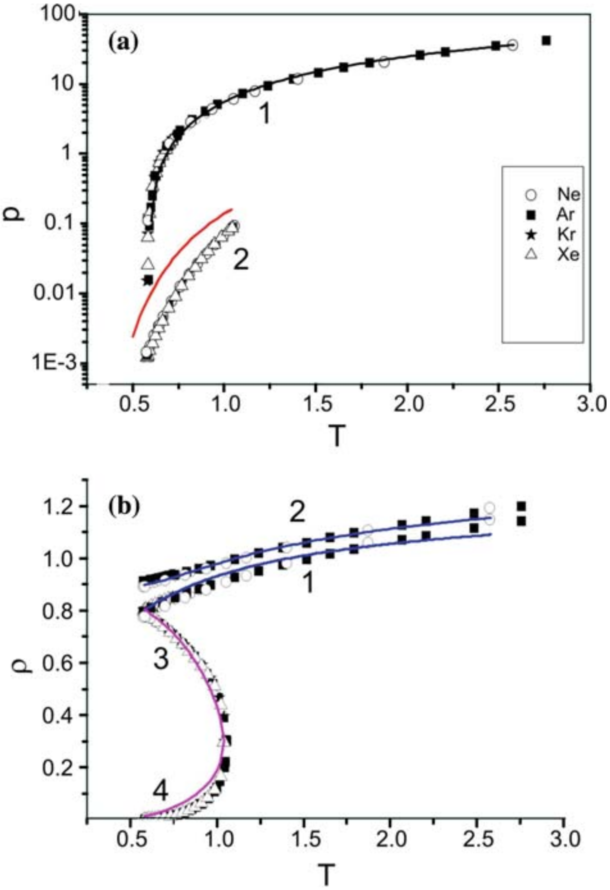

Fig. 1. (a) Reduced pressure and (b) reduced equilibrium densities vs. reduced temperature along the phase coexistence curves. Symbols in (a) correspond to the values of pressure and equilibrium phase densities tabulated for Ne, Ar, Kr, and Xe [4–5]. The same symbols will also be used in other figures. Solid lines are the calculations of this work. In (b), plots 1, 2, 3, and 4 correspond to the solidification curve, melting curve, vaporization curve, and condensation curve, respectively.

We also consider the expression for the free energy of a solid body in the high temperature limit of the Debye theory;

$$F(v,T) = \frac{RT}{\mu} 3 \ln\left(\frac{T_D}{T}\right) + U(v), \tag{5}$$

where $U(v)$ is the potential energy per mass unit.

Using reduced units in Eq. (5), we obtain

$$F^* = 3\ln\left(\frac{3.69Bf(v)\sqrt{2\pi}}{Tv^{1/3}}\right) + U(v) \tag{6}$$

The multiplier 3.69 in Eq. (6) is the mean value of the relation T_D/T_{D0}, found from Table I.

The function $f(v)/v^{1/3}$ corresponds to the dependence of the Debye temperature on volume. We can see that the dependence on the particular substance is determined by the same value 3 $\ln B$ as for the ideal gas.

It has been suggested [10] that the dimensionless entropy $S\mu/R$ (R is the universal gas constant, μ is the atomic weight) of rare gases along all phase coexistence curves can be presented in reduced form as $S^* = S\mu/R + 3\ln B$. As was shown [10], tabulated data for the entropy along all phase coexistence curves are universal functions of the reduced temperature and obey the law of corresponding states.

We note that in the low-temperature limit of the Debye theory,

$$F = \frac{RT}{\mu}\frac{\pi^4}{15}\left(\frac{T}{T_D}\right)^3 + U(v), \tag{7}$$

or in reduced units,

$$F^* = \frac{\pi^4}{15}\left(\frac{T}{3.69Bf(v)\sqrt{2\pi}}\right)^3 + U(v). \tag{8}$$

Here, the variable for the law of similarity is the value T/B. Therefore, the free energy of condensed phases constructed as a function of reduced temperature will depend on the particular substance below the triple point temperature.

4. INTERPOLATION OF THERMODYNAMIC FUNCTIONS

Following earlier work [11], we can write the interpolation formula

$$F_s = 3\ln\left[\frac{B\sqrt{2\pi}}{Tv^{1/3}}\left(3.69f + \sqrt{\frac{T}{2\pi}\frac{1}{e^{1/3}}}\right)\right] + U_s(v) \tag{9}$$

At low temperatures, the second term in the parenthesis is small and Eq. (9) corresponds to the free energy of a crystalline state. On the contrary, at high temperatures and low densities, this term becomes significant, the potential energy is small, and Eq. (9) corresponds to an ideal gas. Thus Eq. (9) describes the interpolation between these states.

When we use a similar formula for the free energy of the liquid, it is necessary to take into account the peculiarity of the latter, connected with its configuration entropy. It is known that the liquid state entropy decreases in a jump during melting due to the higher degree of disorder in the liquid state. The value of this jump in dimensionless units is close to ln 2 [12–14].

To take this into account, we slightly modify Eq. (9) to

$$F_l = 3T\ln\left[\frac{B\sqrt{2\pi}}{Tv^{1/3}}\left(3.69f + \sqrt{\frac{T}{2\pi}\frac{2^{1/3}}{e^{1/3}}}\right)\right] - T\ln 2 + U_l(v) \tag{10}$$

where U_{l} is the potential energy of the liquid state, differing from the potential energy of the solid state U_{s} in Eq. (9). Equation (10) provides a high value of the configurational entropy of the liquid state at small values of the specific volume in comparison with the solid and indicates the transition to the ideal-gas state at large values of the specific volume and temperature. So this expression can be applied for a description of both the liquid and gas states, vaporization and condensation curves, and other liquid–gas thermodynamic parameters.

We note that the representation of the liquid free energy in the form of Eq. (9) assumes the absence of long-range order in the liquid state and the existence of the liquid as a metastable phase under temperatures below the triple point temperature.

Let us write out the formulae for entropy, pressure, internal energy, and specific heat at constant volume, following from Eqs. (9) and (10). The entropy is

$$S_s = 3\left(1 - \frac{1}{2(1+L_s)}\right) - 3\ln\left[\left(\frac{1}{e}\right)^{1/3}\frac{1}{v^{1/3}\sqrt{T}}\left(1+\frac{1}{L_s}\right)\right], \tag{11}$$

$$S_l = 3\left(1 - \frac{L_l}{2(1+L_l)}\right) - 3\ln\left[\left(\frac{2}{e}\right)^{1/3}\frac{1}{v^{1/3}\sqrt{T}}\left(1+\frac{1}{L_l}\right)\right] + \ln 2 \tag{12}$$

The pressure is

$$P_s = \frac{T}{v}\left(1 + 3\frac{\Gamma}{1+L_s}\right) + \Pi_s(v), \tag{13}$$

$$P_l = \frac{T}{v}\left(1 + 3\frac{\Gamma}{1+L_l}\right) + \Pi_l(v), \tag{14}$$

where

$$L = \sqrt{\frac{T}{2\pi}} \frac{a}{3.69f} \tag{15}$$

The value $a = (1/e)^{1/3}$ for L_s, and $a = (2/e)^{1/3}$ for L_l, $\Gamma = -\partial \ln f / \partial \ln v$, and $\Pi = -dU/dv$ is the cold contribution to the pressure.

The energy for the solid and liquid phases has the form,

$$E = 3T\left(1 - \frac{L}{2(1+L)}\right) + U \tag{16}$$

The specific heat at constant volume is

$$c_v = 3\left[1 - \frac{L}{2(1+L)}\left(1 + \frac{1}{2(1+L)}\right)\right] \tag{17}$$

In Eqs. (9)–(13), the quantity L is proportional to the ratio between the mean-square amplitude of thermal vibrations and the square of the mean interparticle distance. This is an analog of the Lindeman parameter from the theory of melting. It is easy to verify that Eqs. (9), (10), (13), (14), (16), and (17) correspond to the Debye theory when the value of L is small. The equations reduce to formulae for the free energy, entropy, pressure, energy, and specific heat of an ideal gas when the values of L are large.

5. DETERMINATION OF THE DEBYE TEMPERATURE AND COLD CONTRIBUTIONS OF PRESSURE FROM TABULAR DATA

Eqs. (6), (9), and (10) contain an unknown function $f(v)$. This function can be determined from the condition that the entropy calculated according to Eqs. (11) and (12) must be equal to the tabulated data [4, 5], for the entropy S_e along the coexistence curves of different phases, i.e., we find $f(v)$ from the solution of equation $S_e = S(T, v, f)$. The values of the function f found in this way for solidification, melting, vaporization, and condensation curves are presented in Fig. 2. They are seen to lie on a universal curve, which can be approximated by the expression,

$$f(v) = 0.5v^{-(1+1.8/v)} \tag{18}$$

This approximation is presented as the solid line in Fig. 2. In this case, the coefficient Γ entering in Eqs. (13) and (14) for pressure has the form,

$$\Gamma = \frac{1.8}{v}(1 - \ln v) + 1 \tag{19}$$

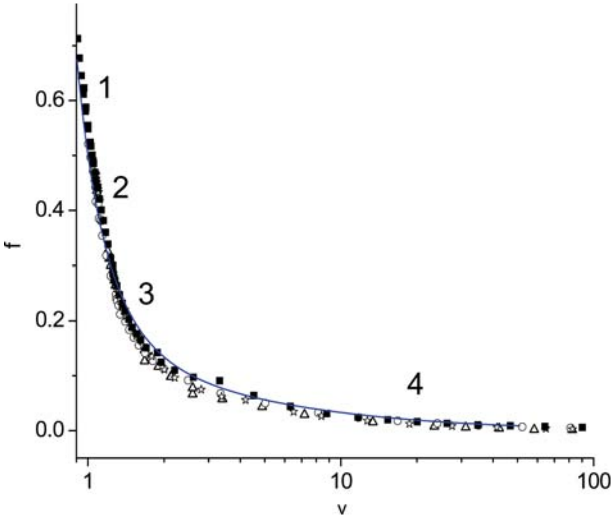

Fig. 2. Dependence of $f(v)$ vs. volume. Symbols correspond to the values of this function obtained on the basis of the tabulated values of entropy for Ne, Ar, Kr, and Xe [4, 5]. Solid line is the approximation of Eq. (18).

We obtained Eqs. (18) and (19) solving the equation $S_e = S(T, v, f)$ along the coexistence lines. We assume that these dependences are valid not only along the coexisting lines. That assumption will be reflected in the fact that the characteristic Debye temperature depends mainly on specific volume and to a lesser degree on temperature. The validity of this assumption will be confirmed by calculations which will be done below.

Now, using the tabulated values of the pressure P_e along the same phase coexistence curves, we can find the potential contribution to pressure (cold part of the pressure) from the solution of the equation $\Pi = P_e - P_T$, where P_T is the thermal contribution to the pressure. The results of such a calculation are presented in Fig. 3. The points obtained from tabulated data along the melting (2), vaporization (3), and condensation (4) curves lie on a unified curve with some dispersion. The points for neon slightly deviate from this common dependence, because this substance has the largest value of the de Boer parameter. The points obtained from the solid state (solidification curve 1) form the repulsive branch of the corresponding potential curve for pressure. We approximate, with a binomial expression, the potential curves for pressure,

$$\Pi(v) = \frac{lkD_1}{(l-k)v}\left[\left(\frac{v_0}{v}\right)^l - \left(\frac{v_0}{v}\right)^k\right] \tag{20}$$

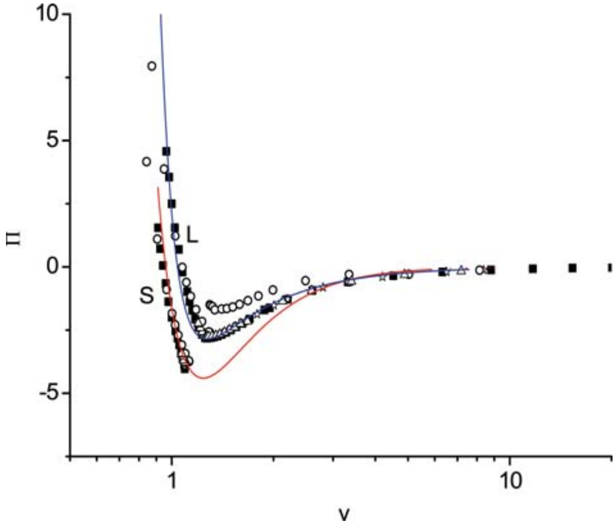

Fig. 3. Symbols are the cold contribution of pressure, found from the tabulated data for Ne, Ar, Kr, and Xe [4, 5]. Solid line "S" is the approximation of Eq. (20) for the solid phase, "L"-for liquid.

The corresponding expression for the potential energy has the form,

$$U(v)=\frac{D_1}{l-k}\left[\left(\frac{v_0}{v}\right)^l k-\left(\frac{v_0}{v}\right)^k l\right] \tag{21}$$

The approximation parameters found from the condition of the best agreement with the tabulated data are given in Table II.

Cold pressure curves constructed according to $\Pi=P_e-P_T$, with the parameters noted in Table II, are drawn in Fig. 3 as solid lines. We note that the potential part of the pressure found for the solid phase corresponds very closely to that calculated with the Lennard–Jones potential [15], provided that only the interaction between nearest neighbors is taken into account. In the latter case, the parameters of the potential are equal to $l=4$, $k=2$, and $D_1=6$. The parameters of the cold curve for the liquid phase differ significantly from the Lennard–Jones values. This is a much stronger repulsive part ($\sim 1/v^9$ instead of $\sim 1/v^4$). On the contrary, the attractive part is more sloping ($\sim 1/v$ instead of the dependence $\sim 1/v^2$ which follows from the Lennard–Jones consideration [15]). The empirical dependence on the volume for the branch of the cold liquid pressure ($\sim 1/v^2$), responsible for the attraction, coincides with the value obtained from the van der Waals equation.

Table II. Values of the Empirical Parameters for the "Cold" Pressure and Potential Energy

State	D_1	l	k	v_0
Solid (S)	5.655	4	2	0.96
Liquid (L)	4.93	9	1.0	1.04

6. RESULTS OF CALCULATIONS AND THEIR DISCUSSION

Let us check to see if we are correct in describing the thermodynamic functions of corresponding states using the interpolation expressions for the free energy and pressure for the solid phase Eqs. (9) and (13) and liquid–gas states Eqs. (9) and (14). The isotherms of the dimensionless free energy calculated according to Eqs. (9) and (10) for $T = 0.58$ (this is the triple point temperature) are shown in Fig. 4. Curve "S" in this figure corresponds to crystalline states and curve "L" to liquid states. The slope of the common tangent to these isotherms determines the phase equilibrium pressure and the values of the volumes at the phase equilibrium. The touching line is practically horizontal. This fact corresponds to a zero

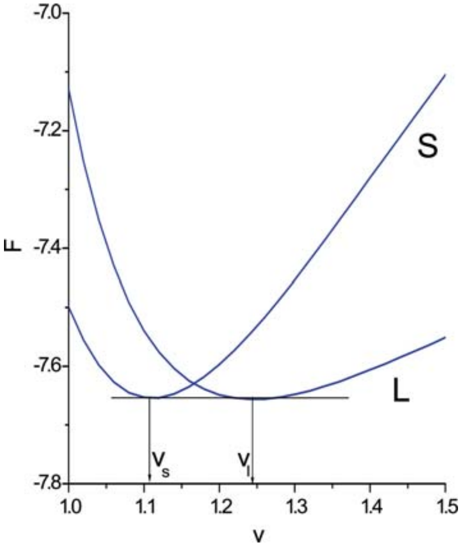

Fig. 4. Dependence of the free energy for solid "S" and liquid "L" phases on volume at the triple point temperature ($T = 0.58$).

value of the pressure at the triple point. The experimental value of this pressure is equal to $p_{\mathrm{tr}} \sim 0.001$ (see Table I). The values of the specific volumes at equilibrium are $v_s \approx 1.1$ and $v_l \approx 1.24$. These data are in good agreement with experimental data (see Table I).

The calculated critical isotherm of pressure is drawn in Fig. 5 for $T = 1.04$. It has a horizontal part, and its inflection point corresponds to the experimental value of the specific volume at the critical point ($v_c = 3.3$). The calculated value of the pressure at the critical point is ~0.16. The experimental value is somewhat lower, ~0.093.

We also calculated the liquid–gas coexistence curve-binodal. The parameters of this curve are found from the equations $F_l(T, v_1) + P_l v_1 = F_l(T, v_2) + P_l v_2$; $P_l(T, v_1) = P_l(T, v_2)$. The values found for the pressure and phase densities are drawn in Fig. 1 as solid lines. As is seen, the densities of the liquid and gas phases are close to the tabulated values. The pressure curve goes somewhat higher than experimental data. This is connected with the binodal pressure for the group of substances under consideration, which is small in comparison with the thermal and cold contributions to pressure.

As a whole, the thermodynamics of corresponding states built on the basis of the interpolation Eqs. (7) and (8) describe the totality of the phase states for temperatures exceeding the triple point temperature with an accuracy sufficient for many applications.

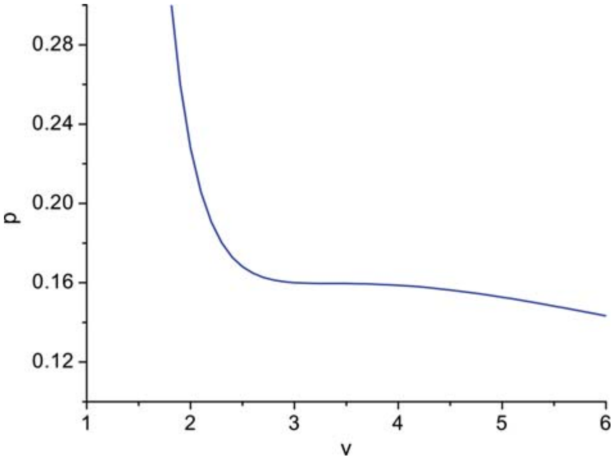

Fig. 5. Calculated critical isotherm ($T = 1.04$).

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