SINGLE EQUATION OF STATE FOR FREON-23 ACCOUNTING FOR FEATURES OF THE CRITICAL REGION

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UDC 536.71

Freon-23 is used as an example to analyze the possibilities of a method proposed earlier to construct a single equation of state for a liquid and gas.

Investigators have recently been paying attention to the problem of constructing an equation of state for a liquid and gas which takes into account the singular character of the critical region. Great successes have been achieved with scale-theory (ST): an equation of state has now been derived which qualitatively accurately communicates the features of the critical region and satisfactorily describes available empirical data in a certain neighborhood of the critical point [1-3]. However, analysis shows that the working range of the ST equation is very narrow [3]. One way of possibly expanding the working range of equations of state of this type is introducing a regular or "background" component [4-7] into its structure. Such an approach makes it possible to significantly expand the range of application of the equation of state. Nevertheless, the authors of the above-noted works did not succeed in solving the problem of constructing an equation of state which takes into account the features of the critical region and at the same time meets the basic requirements for a unique equation of state [8].

The studies [9-11] developed a method of constructing a unique equation of state of a gas and liquid which qualitatively reflects the singular nature of the critical region. The equation of state constructed on the basis of this method is nonanalytical in character and has the form [9]:

$$p(\rho,\ T) = p_s(T_s)\,\frac{T}{T_s(\rho)} + \rho^2 T\left\{\sum_{i=1}^{I}\sum_{n\neq-1}^{i}\frac{A_{in}i}{n+1}\left[1-\frac{T^{n+1}}{T_s^{n+1}(\rho)}\right]+\right.$$

$$\left.+\frac{u'_\mu(\rho)}{T}\left(1-\frac{T}{T_s(\rho)}\right)-\left(f'(\rho)\,F_1(\alpha)+f'_1(\rho)\,F_1(2-\gamma)\right)+f(\rho)\,F_2(\alpha)+f_1(\rho)\,F_2(2-\gamma)\right\}, \tag{1}$$

where

$$F_1(x) = \frac{1}{(2-x)T_g(\rho)}\left[\left(1-\frac{T_g(\rho)}{T}\right)^{2-x}-\left(1-\frac{T_g(\rho)}{T_s(\rho)}\right)^{2-x}\right], \tag{2}$$

$$F_2(x) = \frac{T'_g(\rho)}{(2-x)\,T_н^2(\rho)}\left[\left(1-\frac{T_g(\rho)}{T}\right)^{1-x}\left(1+\frac{T_g(\rho)}{T}(1+x)\right)-\left(1-\frac{T_g(\rho)}{T_s(\rho)}\right)^{1-x}\left(1+\frac{T_g(\rho)}{T_s(\rho)}(1+x)\right)\right. \tag{3}$$

The functions $p_s(T_s)$ and $T_s(\rho)$ in Eq. (1) describe the liquid–vapor equilibrium line; the structure of these functions was chosen with allowance for the features of the corresponding curve in the neighborhood of the critical point:

$$\ln\left[\frac{p_s}{p_k}\right] = B_{-1}\left(\frac{1}{\tilde{T}_s}-1\right)+B_1(\tilde{T}_s-1)+B_2(1-\tilde{T}_s)^{2-\alpha}+B_3(\tilde{T}_s^3-1), \tag{4}$$

$$\tilde{T}_s(\rho) \equiv \frac{T_s(\rho)}{T_k} = 1-D_s|\Delta\rho|^{1/\beta}+\sum_{n\geqslant4}D_n^{\pm}\Delta\rho^n. \tag{5}$$

The curve of the singularity $T_g(\rho)$ is set of points in which the analytic continuation of the relation $c_v(\rho,\ T)$ along an arbitrary isochore becomes infinite. It was shown by the analysis in [9] that this curve lies in the region of the two-phase state, except for the case of critical density. The relation $T_g(\rho)$ is assigned in a form similar to (5):

Leningrad Engineering Institute of the Refrigeration Industry. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 47, No. 4, pp. 602-608, October, 1984. Original article submitted May 31, 1983.

0022-0841/84/4704-1183$08.50

$$T_g(\rho) = T_k\left(1 - E_g|\Delta\rho|^{1/\beta} + \sum_{n\geq 4} E_n^{\pm}\Delta\rho^n\right). \tag{6}$$

The + sign with the coefficients $D_n^{\pm}$ and $E_n^{\pm}$ in the last two relations pertains to the densities $\rho > \rho_k$, while the − sign pertains to the densities $\rho \leqslant \rho_k$.

The function $u_\mu(\rho)$ is chosen on the condition of the equality of the chemical potentials on both branches of the phase equilibrium line. Its specific form is unambiguously determined by the structure of the equation of state [9]:

$$u_\mu(\rho) = \begin{cases} 0 & \text{at } \rho \leqslant \rho_k, \\ \Phi(\rho) & \text{at } \rho > \rho_k, \end{cases} \tag{7}$$

where

$$\Phi(\rho) = \sum_{i=1}^{I}\sum_{n\neq -1}^{i} \frac{A_{in}}{T_s^n}[(\rho^d(\rho))^i - \rho^i] - \left(\frac{1}{\rho^d(\rho)} - \frac{1}{\rho}\right)\left(\frac{dp_s}{dT_s} - \frac{p_s}{T_s}\right)T_s + f(\rho^d(\rho))\left(1 - \frac{T_g(\rho^d(\rho))}{T_s}\right)^{1-\alpha} +$$

$$+ f_1(\rho^d(\rho))\left(1 - \frac{T_g(\rho^d(\rho))}{T_s}\right)^{\gamma-1} - f(\rho)\left(1 - \frac{T_g(\rho)}{T_s}\right)^{1-\alpha} - f_1(\rho)\left(1 - \frac{T_g(\rho)}{T_s}\right)^{\gamma-1}. \tag{8}$$

Finally, the functions $f(\rho)$ and $f_1(\rho)$ in (1) were assigned as follows:

$$f(\rho) = \sum_{n=1} W_n[(\Delta\rho)^n - (-1)^n] - \sum_{n=2} V_n(-1)^n,\ f_1(\rho) = \sum_{n=2} V_n(\Delta\rho)^n. \tag{9}$$

The equation of state (1) derived by the method examined here satisfies two asymptotes [9]. In the case of low densities ($\rho \to 0$), the equation of state reduces to the equation of state of a perfect gas. At the same time, the relations predicted by scale theory follow from Eq. (1) in the asymptotic neighborhood of the critical point. All this on the whole gives hope that an equation of state constructed within the framework of the proposed approach will reliably describe not only the regular region of states but also the region adjacent to the liquid–vapor equilibrium line — including in the neighborhood of the critical point.

The above-described method was used to construct an equation of state for Freon-23. This substance was chosen for study because there is reliable empirical data on its thermal properties both in the single-phase region and on the phase equilibrium line. The latter fact is of no small importance, since the saturation curve is a reference curve in the given approach and the quality of the approximation of the thermal data along the equilibrium curve has a substantial effect on the accuracy of the equation of state.

In constructing equations describing the phase equilibrium (4) and (5), the following empirical data was used for reference: empirical data from the Moscow Energy Institute [12] on the saturated vapor pressure and data from [13] on orthobaric densities.

A specially developed program was used along with the above-noted data to find optimum sets of coefficients for Eqs. (4) and (5) [14]. Here, the critical indices α and β and the critical parameters had the following values: $\alpha = 0.112$, $\beta = 0.342$ [15], $T_k = 298.98$ K, $\rho_k = 525.5$ kg/m³ [13], $p_k = 4.793$ MPa.

The resulting equation of the elasticity line (4) approximates the test data with a mean square error of 0.09%. For comparison, we note that the expression for $p_s(T_s)$ obtained in [16] and containing eight coefficients describes the same data with an error of 0.04%. An important feature of Eq. (4) is that, in contrast to the equation in [16], it is thermodynamically valid at both low saturation temperatures and in the critical region. This observation also pertains to Eq. (5) for the saturation line. The fact that Eqs. (4) and (5) take into account features of the critical region means that equation of state (1), including $p_s(T_s)$ and $T_s(\rho)$ as structural elements, will qualitatively accurately describe the liquid–vapor equilibrium line in the neighborhood of the critical point.

The mean-square error of the approximation of the density of liquid Freon-23 in the saturation state by means of (5) is 0.10%; the approximation of the vapor branch of the phase equilibrium line is more complicated; the error gradually increases as temperature decreases.

TABLE 1. Isochore Heat Capacity of Freon-23

T, K	c_v, $\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$	T, K	c_v, $\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$	T, K	c_v, $\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$
Isochore $\rho_1 = 439{,}9$ kg/m³					
302,08	1,177	307,43	0,9707	314,18	0,9317
302,74	1,096	309,21	0,9632	316,04	0,9294
303,41	1,050	311,70	0,9394	317,67	0,9187
304,15	1,041	312,65	0,9348	319,02	0,9207
305,07	1,020	313,60	0,9281		
Isochore $\rho_2 = 3834$ kg/m³					
302,16	1,051	306,97	0,9597	314,00	0,9233
302,42	1,049	307,74	0,9497	315,03	0,9172
302,72	1,020	308,51	0,9488	316,07	0,9145
303,16	1,015	309,28	0,9442	317,11	0,9122
303,67	1,000	310,06	0,9383	318,13	0,9092
304,17	0,9921	310,81	0,9377	319,15	0,9072
304,67	0,9761	311,61	0,9304		
305,26	0,9743	312,97	0,9245		
Isochore $\rho_3 = 604{,}0$ kg/m³					
299,31	1,311	301,91	1,042	309,15	0,9591
299,53	1,248	302,88	1,046	309,95	0,9481
299,76	1,181	303,47	1,030	310,74	0,9424
300,06	1,141	304,23	1,009	312,28	0,9388
300,45	1,107	304,99	0,9961	313,53	0,9280
300,91	1,084	305,76	0,9814	314,97	0,9261
301,40	1,100	306,53	0,9762		

With the equations derived, a reference curve can be used to optimize the set of coefficients of equation of state (1). The main part of the mass of reference data consisted of thermal parameters of Freon-23 obtained at the Moscow Energy Institute [12, 17]. This data may also be sufficient to construct an equation of the form (1). However, it is best to have additional information on the isochore heat capacity of Freon-23. This is because Eq. (1) contains structural function $T_g(\rho)$, which takes into account features of the behavior of $c_v(\rho, T)$ in the neighborhood of the liquid—vapor equilibrium line. Moreover, it is preferable to have data both in the immediate vicinity of the phase equilibrium line: this will make it possible to determine the character of the relation $T_g(\rho)$ with the most reliability.

There is no empirical data on the isochore heat capacity of Freon-23 in the single-phase state. We therefore attempted to experimentally study c_v in the region adjacent to the liquid—vapor equilibrium line. The work was done in the TOTKhT department of the Leningrad Engineering Institute of the Refrigeration Industry on a unit which employs the method of adiabatic calorimetry with discrete heat input [18]. We studied the isochore heat capacity of Freon-23 on three isochores, two of which corresponded to densities less than the critical value. The resulting empirical data is shown in Table 1. Analysis showed that the error of the values of c_v depends mainly on the size of the calorimetric step and lies in the range 0.4–1.5%.

The data in Table 1, along with the results from [12, 17] within the range $258 \leqslant T \leqslant 393$°K, $\rho \leqslant 2\rho_k$, was included in our reference data file that was used to look for coefficients for equation of state (1). The coefficients of Eq. (1) were given the following values as a result of computer analysis:

$$a_{1,-7} = -2{,}4076287\cdot 10^5; \quad a_{1,-6} = 1{,}2917221\cdot 10^5;$$

$$a_{1,-5} = -2{,}8265842\cdot 10^6;\ a_{1,-4} = 3.2601461\cdot 10^6;\ a_{1,-3} = -2.1366067\cdot 10^6;$$
$$a_{1,-2} = 7.4342062\cdot 10^5;\ a_{10} = -1.4147963\cdot 10^5;\ a_{11} = 4.9814096\cdot 10^4;\ a_{2,-6} =$$
$$= 4{,}9376695\cdot 10^5;\ a_{2,-5} = -4.5418480\cdot 10^6;\ a_{2,-4} = 1.7238141\cdot 10^7;\ a_{2,-3} =$$
$$= -3.2697761\cdot 10^7;\ a_{2,-2} = 2{,}8377354\cdot 10^7;\ a_{20} = -2{,}0291958\cdot 10^7;\ a_{21} =$$
$$= 1.4980065\cdot 10^7;\ a_{22} = -3{,}5559257\cdot 10^6;\ a_{3,-5} = -1.1486627\cdot 10^7;\ a_{3,-4} =$$
$$= 7.9699429\cdot 10^7;\ a_{3,-3} = -2.1535465\cdot 10^8;\ a_{3,-2} = 2.4937902\cdot 10^8;\ a_{30} =$$
$$= -3.3269797\cdot 10^8;\ a_{31} = 3{,}8253858\cdot 10^8;\ a_{32} = -1.8776697\cdot 10^8;\ a_{33} =$$
$$= 3{,}5684833\cdot 10^7;\ a_{4,-4} = 8.6834125\cdot 10^6;\ a_{4,-3} = -5.4662654\cdot 10^7;\ a_{4,-2} =$$
$$= 1.1258988\cdot 10^8;\ a_{40} = -3.8447485\cdot 10^8;\ a_{41} = 7.1247464\cdot 10^8;\ a_{42} =$$

TABLE 2. Standard Deviations of Values of the Density of Freon-23 Calculated along Isotherms from Equation of State (1) from Test Data Obtained at the Moscow Energy Institute

Isotherm T, K	$\delta\rho^{av}$, %	Isotherm T, K	$\delta\rho^{av}$, %	Isotherm T, K	$\delta\rho^{av}$, %
393,15	0,65	323,15	0,48	298,06	0,41
373,15	0,46	313,15	0,94	293,15	0,63
353,15	0,57	303,15	0,87	283,15	0,55
343,15	0,39	300,15	0,32	278,15	0,39
333,15	0,40	299,15	0,38	273,15	0,63

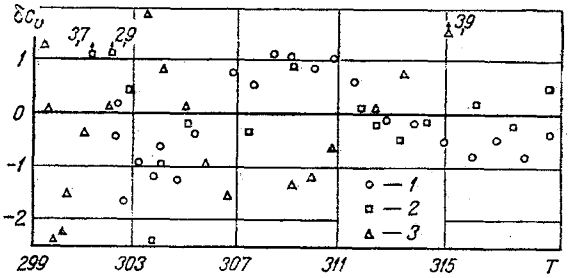

Fig. 1. Deviation of values of isochore heat capacity calculated from equation of state (1) from test data: 1) isochore $\rho = \rho_1$; 2) $\rho = \rho_2$; 3) $\rho = \rho_3$. T, K; δc_v, %.

$$
\begin{gathered}
= -6.1466764\cdot10^8;\ a_{43} = 2.6747498\cdot10^8;\ a_{44} = -4.7412555\cdot10^7;\ a_{5,-2} = \\
= 1.1489833\cdot10^6;\ a_{50} = -2.9524729\cdot10^7;\ a_{51} = 1.0653433\cdot10^8;\ a_{52} = \\
= -1.7050173\cdot10^8;\ a_{53} = 1.4355564\cdot10^8;\ a_{54} = -6.2202512\cdot10^7;\ a_{55} = \\
= 1.0987449\cdot10^7;\ a_{6,-4} = -2.6615904\cdot10^4;\ a_{6,-2} = 2.0004421\cdot10^5;\ a_{60} = \\
= -5.5397592\cdot10^5;\ a_{62} = 6.7322754\cdot10^5;\ a_{64} = -3.3795537\cdot10^5;\ a_{66} = \\
= 4.4384383\cdot10^4;\ a_{70} = -3.1068124\cdot10^4;\ a_{71} = 7.0914276\cdot10^4;\ a_{73} = \\
= -3.6897493\cdot10^4;\ a_{75} = -3.5181773\cdot10^4;\ a_{77} = 3.4213669\cdot10^4;\ a_{80} = \\
= -1.2703225\cdot10^3;\ a_{82} = 2.0202990\cdot10^3;\ a_{84} = -1.4628912\cdot10^4;\ a_{86} = \\
= 2.8969878\cdot10^4;\ a_{88} = -1.6221294\cdot10^4;\ a_{90} = 1.3176843\cdot10^2;\ a_{93} = \\
= 1.0913517\cdot10^3;\ a_{96} = -2.5308840\cdot10^3;\ a_{99} = 1.6032375\cdot10^3;\ a_{10,0} = \\
= -4.0459510\cdot10^1;\ a_{10.5} = 7.0700982\cdot10^1;\ a_{10,10} = -6.1102788\cdot10^1;\ w_1 = \\
= 2.368699\cdot10^1;\ w_2 = 7.695965\cdot10^2;\ w_3 = 1.170967\cdot10^3;\ w_4 = 4.113472\cdot10^2; \\
v_2 = -2.259816\cdot10^1;\ v_3 = 8.389933\cdot10^0;\ v_4 = -1.118433\cdot10^1;\ E_g = 0.230; \\
E_n^+ = 0;\ E_6^- = -0.770.
\end{gathered}
$$

As noted earlier, the main goal of this article was to examine the possibility of using Eq. (1) to describe with equal accuracy both the regular and singular parts of the thermodynamic surface. Table 2 shows results which characterize the accuracy of the calculation of density along near-critical isotherms and isotherms located far from the critical point. It is apparent that the error of the description of the density of Freon-23 is practically the same on all of the isotherms. Thus, the problem of a sharp difference in the accuracy of the description of the regular and irregular parts of a thermodynamic surface, typical of analytic equations of state, can be solved within the framework of the proposed approach. This also applies to the description of thermal surface and (to an even greater degree) to calculation of the isochore heat capacity (see Fig. 1).

The above method was used in [9] to construct a single equation of state of a gas and liquid using the example of argon. As in the present work, in [9] it was shown to be basically possible to use a single equation of state to describe an entire thermodynamic surface with almost equal accuracy, including the neighborhood of the critical point. It was therefore demonstrated that the method is applicable not only to substances with a simple molecular structure (such as argon) but also to substances with a complex molecular structure (molecules of Freon-23, for example, have a dipole moment equal to 1.65 ± 0.09).

The main shortcoming of equation of state (1) is that the standard deviation of the description of the thermal data is relatively high — around 0.6%. For comparison, we note that in the case of the analytic equation in [16] the following was obtained for the same empirical data: $\delta\rho^{av} = 0.2\%$.

The fact that Eq. (1) is not quite completely satisfactory for calculating thermal parameters compels us to examine two issues: first, to determine the reason for this and, second, to determine if it is possible to improve the accuracy of the equation.

An analysis showed that the shortcoming pointed out is not an indictment of the method used to obtain the equation but is instead related to the specific selection of the form of the structural functions in Eq. (1). A future task is to search for ways of improving the given approach. However, we can already point to the basic directions to be taken in solving the problem. First, it is evident that the method of describing the vapor branch of the saturation line in the form of (5) is far from ideal. Second, the structure of the regular part of the equation of state will have to be further analyzed. Finally, the accuracy of the equation would be increased by allowing for nonasymptotic terms in the expression for intrinsic energy, which is the basis for the derivation of the equation of state.

NOTATION

p, pressure; ρ, density; T, absolute temperature; T_s, saturated vapor temperature; p_s, pressure of substance in saturated state; α, β, γ, critical indices; $T_g(\rho)$, $f(\rho)$ and $f_1(\rho)$, structural functions of intrinsic energy; u, intrinsic energy; $\tilde{T}_s = T_s/T_k$; p_k, ρ_k, T_k, critical parameters; B_i, coefficients of the equation of the elasticity line; D_s and $D_n^\pm$, coefficients of the equation of the saturation line; E_g and $E_n^\pm$, coefficients of the curve of the singularity $T_g(\rho)$; ρ^d, density of the saturated vapor; c_v, isochore heat capacity; δ_ρ, deviation of calculated value of density ρ^t from reference data, $\delta\rho = (\rho^{re} - \rho^t)/\rho^{re}\, 100\%$; $\delta_\rho{}^{av} = \left[\left(\sum_{n=1}^{N} \delta\rho_n^2\right)/N\right]^{1/2}$; N, number of experimental points; $\delta c_v = (c_v^{re} - c_v^t)/c_v^{re} \cdot 100\%$; A_{in}, W_n, and V_n, coefficients of the equation of state; $a_{in} = A_{in}\rho_k^{i+1}/(p_k T_k^n)$, $w_n = W_n\rho_k/\rho_k$, $v_n = V_n\rho_k/\rho_k$.

LITERATURE CITED

1. M. A. Anisimov, "Studies of critical phenomena in liquids," Usp. Fiz. Nauk, 114, No. 2, 249-294 (1974).
2. M. Vicentini-Missoni, J. M. H. Levelt-Sengers, and M. S. Green, "Scaling analyzing of thermodynamic properties in the critical region of fluids," J. Res. Nat. Bur. Stand., 73A, No. 6, 563-568 (1969).
3. V. A. Rabinovich, A. A. Vasserman, B. A. Koval'chuk, and A. T. Berestov, "Evaluating the possibility of using a virial equation of state to calculate thermodynamic functions of pure substances near the critical point," in: Thermophysical Properties of Substances and Materials [in Russian], Vol. 13, Standartov, Moscow (1979), pp. 24-39.
4. O. B. Verbeke, V. Jansoone, H. Gielen, and J. De Boelpaep, "The equation of state of fluid argon and calculation of the scaling exponents," J. Phys. Chem., 73, No. 12, 4076-4085 (1969).
5. V. A. Rabinovich and Yu. E. Sheludyak, "Method of constructing the equation of state in a broad neighborhood of the critical point," in Thermophysical Properties of Substances and Materials, Vol. 16, Standartov, Moscow (1982), pp. 108-124.
6. Kh. I. Amirkhanov, I. M. Abdulagatov, and B. G. Alibekov, "Equation of state of liquid n-pentane based on measurements of isochore heat capacity," Zh. Fiz. Khim., 55, No. 2, 341-346 (1981).
7. I. M. Abdulagatov and B. G. Alibekov, "Construction of a generalized equation for the caloric ($C_v^* - \varphi - \tau$) surface of n-alkanes in a broad neighborhood of the critical point," Zh. Fiz. Khim., 57, No. 2, 438-439 (1983).
8. V. V. Altunin, Thermophysical Properties of Carbon Dioxide [in Russian], Standartov, Moscow (1975).
9. V. F. Lysenkov and E. S. Platunov, "Structure of a single equation of state considering features of the behavior of the substance in the near-critical region," Teplofiz. Vys. Temp., 21, No. 4, 673-679 (1983).
10. V. F. Lysenkov and E. S. Platunov, "Equation of state considering features of intrinsic energy," Teplofiz. Vys. Temp., 19, No. 3, 507-513 (1981).
11. E. S. Platunov, V. F. Lysenkov, and N. V. Vas'kova, "Use of two reference curves to construct the equation of state of a gas and liquid," Teplofiz. Vys. Temp., 20, No. 2, 249-254 (1982).

12. D. S. Rasskazov, E. K. Petrov, G. A. Spiridonov, and É. R. Ushmaikin, "Study of the p–V–T relation of Freon-23," in: Thermophysical Properties of Substances and Materials [in Russian], Vol. 8, Standartov, Moscow (1975), pp. 4-16.
13. A. M. Shavandrin, N. M. Potapova, and Yu. R. Chashkin, "Study of an existence curve by the method of quasistatic thermograms," in: Thermophysical Properties of Substances and Materials [in Russian], Vol. 9, Standartov, Moscow (1976), pp. 141-146.
14. N. V. Vas'kova, "Equation of the saturation line and elasticity curve of Freon-23," in: Analysis and Improvement of Machines and Apparatuses for Refrigeration, Cryogenics, and Air Conditioning [in Russian], Leningrad Technological Inst. (1982), pp. 95-97.
15. M. A. Anisimov, A. T. Berestov, V. P. Voronov, et al., "Critical indices of liquids," Zh. Eksp. Teor. Fiz., 76, No. 5, 1661-1669 (1979).
16. S. L. Rivkin (ed.), Thermophysical Properties of Freons, Vol. 1, Methane-Series Freons [in Russian], Standartov, Moscow (1980).
17. D. S. Rasskazov, E. K. Petrov, and É. R. Ushmaikin, "Experimental study of the density of Freon-23 in the liquid phase," Tr. Mosk. Energ. Inst., No. 234, 52-57 (1975).
18. M. A. Anisimov, B. A. Koval'chuk, V. A. Rabinovich, and V. A. Smirnov, "Experimental study of the isochore heat capacity of argon in a broad range of parameters of state, including the critical point," in: Thermophysical Properties of Substances and Materials [in Russian], Vol. 8, Standartov, Moscow (1975), pp. 237-245.