Journal of Engineering Physics and Thermophysics, Vol. 66, No. 3, 1994

NONANALYTICAL UNIFIED EQUATION OF STATE OF FREEZANT R23

V. F. Lysenkov, A. D. Kozlov,
P. V. Popov, and M. V. Yakovleva

UDC 536.71

A unified equation of state of freezant R23 is obtained that adequately describes a thermodynamic surface both in the region of low densities and pressures and in the vicinity of a critical point.

In [1-4] an approach to constructing wide-range equations of state of a gas and a liquid that take into account the distinctive features of the critical region is suggested. The approach is based on the rigorous thermodynamic equality

$$P(\rho, T) = P_s(T_s(\rho))\frac{T}{T_s(\rho)} - \rho^2 T \int\limits_{T_s(\rho)}^{T} \left(\frac{\partial u}{\partial \rho}\right)_T \frac{dT}{T^2}, \tag{1}$$

where $P_s(T_s)$ and $T_s(\rho)$ specify the liquid-vapor phase equilibrium curve; $u = u(\rho, T)$ is the internal energy of the substance; P is the pressure; T is the absolute temperature.

In order to obtain a specific form of the equation of state, it is necessary to have at hand an expression for the internal energy $u(\rho, T)$ as well as equalities specifying the phase equilibrium curve of $P_s(T_s)$ and $T_s(\rho)$. The present work is aimed at derivation of a unified nonanalytical equation of state that is valid in a wide neighborhood of the critical point. This means that the constructed functions $u(\rho,T)$, $P_s(T_s)$, and $T_s(\rho)$ must have a structure such that the following conditions are satisfied:

$$P(\rho \to 0, T) = \frac{R}{M}\rho T + \ldots; \tag{2}$$

the critical conditions

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_{\rm cr}}^{\rho=\rho_{\rm cr}} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_{\rm cr}}^{\rho=\rho_{\rm cr}} = \left(\frac{\partial^3 P}{\partial \rho^3}\right)_{T_{\rm cr}}^{\rho=\rho_{\rm cr}} = \left(\frac{\partial^4 P}{\partial \rho^4}\right)_{T_{\rm cr}}^{\rho=\rho_{\rm cr}} = 0; \tag{3}$$

the Planck-Gibbs rule

$$\left(\frac{dP_s}{dT_s}\right)^{T=T_{\rm cr}} = \left(\frac{\partial P}{\partial T}\right)_{\rho_{\rm cr}}^{T=T_{\rm cr}}; \tag{4}$$

the phase equilibrium conditions

$$P_s^{\rm v}(T_s) = P_s^{\rm liq}(T_s), \quad \mu^{\rm v}(T_s) = \mu^{\rm liq}(T_s); \tag{5}$$

on the critical isochor at $T \to T_{\rm cr}$

Research Center on Materials and Substances of State Standard, St. Petersburg, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 66, No. 3, pp. 321-329, March, 1994. Original article submitted August 11, 1992.

1062-0125/94/6603-0286$12.50 ©1994 Plenum Publishing Corporation

$$\frac{\rho_{\text{cr}} T_{\text{cr}}}{P_{\text{cr}}} C_v = A_0^+ \tau^{-\alpha} + A_1^+ + A_2^+ \tau^{-\alpha+\Delta} + \ldots, \tag{6}$$

$$P_{\text{cr}} K_T = \Gamma_0^+ \tau^{-\gamma} + \Gamma_1^+ \tau^{-\gamma+\Delta} + \Gamma_2^+ \tau^{-\gamma+2\Delta} + \ldots, \tag{7}$$

$$\Delta P = P_0^+ \tau + P_1^+ \tau^{2-\alpha} + P_2^+ \tau^2 + P_3^+ \tau^{2(\beta\delta-1)-1} + \ldots; \tag{8}$$

on the critical isotherm $\rho \to \rho_{\text{cr}}$

$$\Delta P = \pm D_0 \, |\Delta\rho|^{\delta} + D_1 \, |\Delta\rho|^{\delta+1} \pm D_2 \, |\Delta\rho|^{\delta+\frac{\Delta}{\beta}} + \ldots; \tag{9}$$

on the phase equilibrium curve at $T_s \to T_{\text{cr}}$

$$\frac{\rho_{\text{cr}} T_{\text{cr}}}{P_{\text{cr}}} C_v = A_0^- \tau_s^{-\alpha} + A_1^- \pm A_2 \tau_s^{\beta-\alpha} + A_3^- \tau_s^{\Delta-\alpha} + \ldots, \tag{10}$$

$$P_{\text{cr}} K_T = \Gamma_0^- \tau_s^{-\gamma} \pm \Gamma_0^- \tau_s^{\beta-\gamma} + \Gamma_0^- \tau_s^{-\gamma+\Delta} + \ldots, \tag{11}$$

$$\Delta P_s = P_0^- \tau_s + P_1^- \tau_s^{2-\alpha} + P_2^- \tau_s^2 + P_3^- \tau_s^{2-\alpha+\Delta} + \ldots, \tag{12}$$

$$(\rho^{\text{v}} + \rho^{\text{liq}})/(2\rho_{\text{cr}}) = 1 + B_2 \tau_s^{1-\alpha} + B_3 \tau_s + B_5 \tau_s^{1-\alpha+\Delta} + \ldots, \tag{13}$$

$$(\rho^{\text{liq}} - \rho^{\text{v}})/(2\rho_{\text{cr}}) = B_0 \tau_s^{\beta} + B_1 \tau_s^{\beta+\Delta} + B_4 \tau_s^{\beta+2\Delta} + \ldots \tag{14}$$

Here R is the gas constant; M is the molar mass; $P_{\text{cr}}, \rho_{\text{cr}}, T_{\text{cr}}$ are the critical parameters; the superscript "v" pertains to a dry saturated vapor, and "*liq*" to a saturated liquid; μ is the chemical potential; C_v is the specific heat at constant volume; K_T is the isothermal compressibility; $\Delta P = (P-P_{\text{cr}})/P_{\text{cr}}$, $\Delta\rho = (\rho-\rho_{\text{cr}})/\rho_{\text{cr}}$, $\tau = (T-T_{\text{cr}})/T_{\text{cr}}$, $\tau_s = (T_{\text{cr}}-T_s)/T_{\text{cr}}$, $\Delta P_s = (P_{\text{cr}}-P_s)/P_{\text{cr}}$; α, β, γ, δ and Δ are the critical indices determined in the usual manner [5]:

$$\alpha = 0.115 \pm 0.005\,, \quad \gamma = 1.238 \pm 0.011\,, \quad \delta = 4.76 \pm 0.09\,, \quad \beta = 0.321 \pm 0.005\,. \tag{15}$$

Conditions (2)-(14) may be subdivided into two groups. The first group comprises equalities (2)–(5). These conditions are imposed (fully or partially) on the unified analytical equations of state [6-8, etc.]. The second group includes expressions (6)-(15), which follow from the current theory of critical phenomena [9]. The scaled equations of state [10-12] correspond to them fully or partially.

Thus, we have the following situation. The unified analytical equations of state correspond to conditions (2)–(5) but contradict equalities (6)-(15). As a consequence, such equations hold on the regular part of a surface and are not at all applicable upon approaching the critical point. On the other hand, the scaled parametric equations describe correctly the near-critical anomalies and cannot be used beyond a wide vicinity of the critical point [13, 14].

Now Eq. (1) is required to satisfy the entire set of conditions (2) and (15). The structure of this equation contains equations describing the phase equilibrium line of $P_s(T_s)$ and $T_s(\rho)$. These relations must take into account the specific features of the equilibrium curve in the critical region (2)-(15) as well as its shape in the regular region of states:

It is known that with a decrease in the saturation temperature T_s the phase equilibrium curve must correspond to the conditions

$$\frac{dP_s}{dT_s} = \frac{r\rho^{\mathrm{v}}}{T_s} \quad \text{and} \quad P_s\,(T_s) = \frac{R}{M}\rho^{\mathrm{v}} T_s\,, \tag{16}$$

where the heat of the phase transition r tends to some constant value.

All these conditions are appropriate for the following system of equations [15, 16]:

$$\ln \widetilde{P}_s = E_{-1}\left(1 - \frac{1}{\widetilde{T}_s}\right) + E_1\,\tau_s + E_2\,\tau_s^{2-\alpha} + E_3\,\tau_s^2 + E_4\,\tau_s^{2-\alpha+\Delta} + E_5\,\tau_s^3\,, \tag{17}$$

$$\Delta\rho^{\mathrm{liq}} = B_0\,\tau_s^{\beta} + B_1\,\tau_s^{\beta+\Delta} + B_2\,\tau_s^{1-\alpha} + B_3\,\tau_s + B_4\,\tau_s^{\beta+2\Delta} + B_5\,\tau_s^{1-\alpha+\Delta} + B_6\,\tau_s^2 + B_7\,\tau_s^3\,, \tag{18}$$

$$\widetilde{\rho}^{\mathrm{v}} = \frac{\widetilde{P}_s}{\widetilde{T}_s}\,[1 - B_0\,\tau_s^{\beta} - B_1\,\tau_s^{\beta+\Delta} + B_2\,\tau_s^{1-\alpha} + B_3^-\,\tau_s + B_4^-\,\tau_s^{\beta+2\Delta} + B_5\,\tau_s^{1-\alpha+\Delta} + B_6\,\tau_s^6 + B_7^-\,\tau_s^7\,]\,, \tag{19}$$

$$B_3^- = B_3 - E_{11}\,, \quad B_4^- = -\,B_4 + E_{11}\,B_0\,, \quad E_{11} = 1 + E_1 - E_{-1}\,,$$

$$B_7^- = Z_{\mathrm{cr}} - 1 + B_0 + B_1 - B_2 - B_3^- - B_4^- - B_5 - B_6\,, \tag{20}$$

$$Z_{\mathrm{cr}} = P_{\mathrm{cr}}M/(R\rho_{\mathrm{cr}}T_{\mathrm{cr}})\,, \quad \widetilde{P}_s = P_s/P_{\mathrm{cr}}\,, \quad \widetilde{\rho}^{\mathrm{v}} = \rho^{\mathrm{v}}/\rho_{\mathrm{cr}}\,, \quad \widetilde{T}_s = T_s/T_{\mathrm{cr}}\,.$$

It is easy to check that at $T_s \to T_{\mathrm{cr}}$ conditions (12)-(15) follow from (17)-(20) while at $T_s \to 0$ Eqs. (17)-(20) convert to equalities (16). Thus, system of equations (17)-(20) describes the phase equilibrium curve qualitatively correctly both in the critical region and at a distance from it. Equation of state (1) contains the equilibrium curve in its structure and, as a consequence, qualitatively correctly accounts for the specific features of this curve within its domain of definition.

As regards the regular part of a surface, the expression $u(\rho,T)$ is "responsible" for the description of its specific features. It is convenient to single out a number of summands in its structure, each of which plays an independent role:

$$u\,(\rho\,,\,T) = u_0\,(T) + T^2\left\{u_{\mathrm{r}}\,(\rho\,,\,T) + u_{\rho_{\mathrm{cr}}}\,(\rho\,,\,T) + u_{T_{\mathrm{cr}}}\,(\rho\,,\,T) + u_{\mathrm{ir}}\,(\rho\,,\,T)\right\} + u_{\mu}\,(\rho)\,. \tag{21}$$

Here $u_0(T)$ is the internal energy of an ideal gas, $u_{\mathrm{r}}(\rho,\,T)$ indicates formation of the regular part of a surface:

$$\frac{T_{\mathrm{cr}}^2\rho_{\mathrm{cr}}}{P_{\mathrm{cr}}}\,u_{\mathrm{r}}\,(\widetilde{\rho}\,,\,\widetilde{T}\,) = \sum_{n=1}^{N}\sum_{m=1}^{M}\frac{a_{nm}}{\widetilde{T}^{\,n+1}}\left[\tau_s^m - 1 - \frac{n+1}{n}\,\frac{1}{\widetilde{T}}\times\right.$$

$$\left.\times\left(\tau_s^{m+1} - 1 - \frac{m}{m+1}\,(\tau_s^{m+1} - 1)\right)\right]. \tag{22}$$

The summand $u_{\rho_{\mathrm{cr}}}$ takes into account the specific features of the critical isochor:

$$\frac{T_{\mathrm{cr}}^2\rho_{\mathrm{cr}}}{P_{\mathrm{cr}}}\,u_{\rho_{\mathrm{cr}}}\,(\widetilde{\rho}\,,\,T) = \sum_{k=1}^{K}\sum_{l=3}^{L}\,c_{kl}\,\widetilde{\rho}^{\,\mathrm{cr}}\,[\widetilde{T} - \widetilde{T}_s\,(\widetilde{\rho})\,]^{l-1}\,; \tag{23}$$

the summand $u_{T_{\mathrm{cr}}}(\widetilde{\rho}, \widetilde{T})$ is responsible for the shape of the critical isotherm:

$$\frac{T_{\mathrm{cr}}^2 \rho_{\mathrm{cr}}}{P_{\mathrm{cr}}} u_{T_{\mathrm{cr}}} (\widetilde{\rho}\,, T) = g(\widetilde{\rho})\,[A + B\widetilde{T}]\,,$$

$$g(\widetilde{\rho}) = \sum_{i=0}^{4} (\Delta\rho\,|\Delta\rho|^{i} + 1) + \frac{\beta E_2 B_0^{-\frac{1-\alpha}{\beta}}}{(\beta - \alpha + 1)(A + B)} (1 + \Delta\rho\,|\Delta\rho|^{\frac{1-\alpha}{\beta}})\,,$$

$$B = -2\,[1 + E_1 - 2E_2 + E_3 + (E_1 - E_{-1})^2/2]\,, \quad A + B = 1 + E_1 - E_{-1}\,. \tag{24}$$

The irregular component of the internal energy is responsible for specific features of the critical region

$$\frac{T_{\mathrm{cr}}^2 \rho_{\mathrm{cr}}}{P_{\mathrm{cr}}} u_{\mathrm{ir}} (\widetilde{\rho}\,, T) = \sum_{i=0}^{1} \left\{ f_i(\widetilde{\rho}) \left[\frac{\widetilde{T} - \widetilde{T}_{\mathrm{ir1}}(\widetilde{\rho}))^{1-\alpha_i} - \frac{\omega_1}{\omega_2}(\widetilde{T} - \widetilde{T}_{\mathrm{ir2}}(\widetilde{\rho}))^{1-\alpha_i}}{1 - \omega_1/\omega_2} + \right.\right.$$

$$\left.\left. + \varphi_i \tau_s^{2\beta} (\widetilde{T} - \widetilde{T}_{\mathrm{ir},i+3}(\widetilde{\rho}))^{\gamma_i - 1} \right]\right\}, \tag{25}$$

$$\widetilde{T}_{\mathrm{ir}i}(\widetilde{\rho}) = 1 - \omega_i \tau_s\,, \tag{26}$$

$$f_i(\widetilde{\rho}) = \sum_{\varepsilon=1}^{E_i} b_{i\varepsilon} \widetilde{\rho}^{\,\varepsilon}\,, \tag{27}$$

$$\varphi_0 = -\alpha b^2 (1 - \alpha)/(\gamma - 1)\,, \quad \varphi_1 = \gamma_1 b^2 \alpha_1 (1 - \alpha_1)/(\widetilde{\gamma}_1 - 2\beta_1 - b^2 \alpha_1 \gamma_1)\,, \tag{28}$$

where $\alpha_1 = \alpha - \Delta$, $\gamma_1 = \gamma + \Delta$, $\widetilde{\gamma_1} = \gamma - \Delta$, b_2 is the parameter of the linear model responsible for "fixing" of the critical isotherm. The parameters ω_i are universal functions of the critical indices.

Finally, the last summand $u_\mu(\widetilde{\rho})$ in (21) is "responsible" for equality of the chemical potentials of the vapor and the liquid in the saturation state:

$$\widetilde{u}_\mu(\widetilde{\rho}) \equiv \frac{\rho_{\mathrm{cr}}}{P_{\mathrm{cr}}} u_\mu(\rho) = \begin{cases} 0 & \text{when } \widetilde{\rho} \le 1\,, \\ \Phi(\widetilde{\rho}) & \text{when } \widetilde{\rho} > 1\,, \end{cases} \tag{29}$$

$$\Phi(\widetilde{\rho}) = \left[\frac{1}{\widetilde{\rho}^{\mathrm{v}}(\widetilde{\rho})} - \frac{1}{\widetilde{\rho}} \right] \left(\frac{\widetilde{P}_s}{\widetilde{T}_s} - \frac{d\widetilde{P}_s}{d\widetilde{T}_s} \right) \widetilde{T}_s + (A + B\widetilde{T}_s)\,\widetilde{T}_s^{\,2} (g(\widetilde{g}^{\mathrm{v}}(\rho)) -$$

$$- g(\widetilde{\rho})) + \sum_{i=0}^{1} (f_i(\widetilde{\rho}^{\mathrm{v}}(\widetilde{\rho})) - f_i(\widetilde{\rho})) \times$$

$$\times \left[\frac{(\widetilde{T}_s - \widetilde{T}_{\mathrm{ir1}}) - \frac{\omega_1}{\omega_2}(\widetilde{T}_s - \widetilde{T}_{\mathrm{ir2}})^{1-\alpha_i}}{1 - \omega_1/\omega_2} + \varphi_i \tau_s^{2\beta} (\widetilde{T}_s - \widetilde{T}_{\mathrm{ir},i+3})^{\gamma_i - 1} \right]. \tag{30}$$

After substitution of (21) and (30) into (1) and simple transformations we arrive at

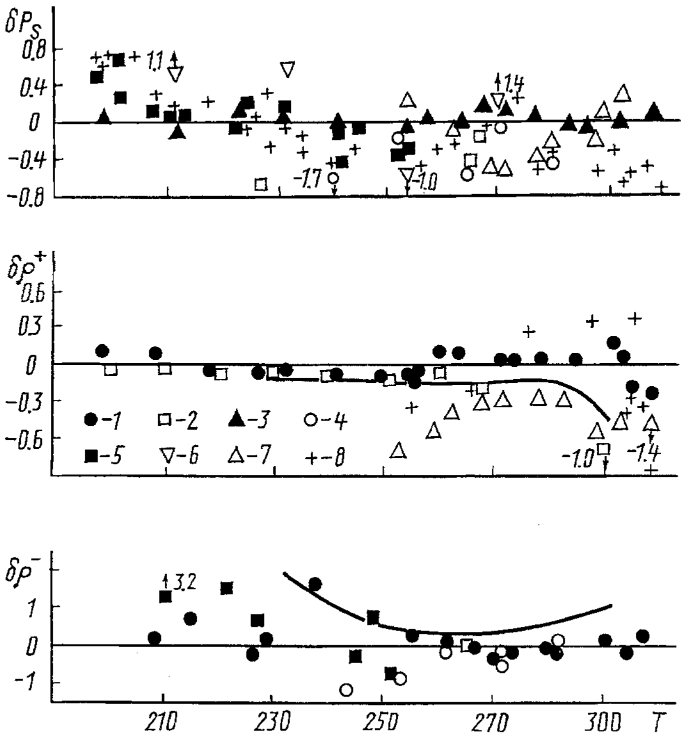

Fig. 1. Deviations of calculated values of P_s, ρ^+, and ρ^- (%) from experimental data: 1) [8]; 2) [19]; 3) [17]; 4) [26]; 5) [27]; 6) [28]; 7) [29]; 8) [30]; solid line, comparison with data calculated by an analytical equation [20]. T, K.

$$\tilde{P}(\tilde{\rho}, T) = \tilde{P}_s(\tilde{T}_s)\frac{\tilde{T}}{\tilde{T}_s} - \tilde{\rho}^2 T \left\{ g'(\Delta\rho)\left[A(\tilde{T} - \tilde{T}_s) + \frac{B}{2}(\tilde{T}^2 - T_s^2)\right] - \right.$$

$$- \left(1 - \frac{\tilde{T}}{\tilde{T}_s}\right)\tau_s' \sum_{n=1}^{N}\sum_{m=2}^{M} a_{nm}\frac{m}{n}\tau_s^{m-1}\tilde{T}^{-n} + \sum_{k=1}^{K}\sum_{l=3}^{L} c_{kl}\tilde{\rho}^{k-1}(\tilde{T} - \tilde{T}_s)^{l-1} \times$$

$$\times \left[\frac{k}{l}(\tilde{T} - \tilde{T}_s) + \tilde{\rho}\tau_s'\right] + \sum_{i=0}^{1}[f_i'(\tilde{\rho})V_i(\tilde{T}) + f_i(\tilde{\rho})W_i(\tilde{T})] +$$

$$\left. + \left(\frac{1}{\tilde{T}_s} - \frac{1}{\tilde{T}}\right)\tilde{u}_\mu(\tilde{\rho})\right\}, \tag{31}$$

where

$$V_i(\tilde{T}) = V_{1i}(\tilde{T}) - V_{1i}(\tilde{T}_s), \quad W_i(\tilde{T}) = W_{1i}(\tilde{T}) - W_{1i}(\tilde{T}_s), \tag{32}$$

$$V_{1i}(x) = \frac{(x - \tilde{T}_{\mathrm{ir1}})^{2-\alpha_i} - \frac{\omega_1}{\omega_2}(x - \tilde{T}_{\mathrm{ir2}})^{2-\alpha_i}}{(2 - \alpha_i)(1 - \omega_1/\omega_2)} + \frac{\varphi_i}{\gamma_i}\tau_s^{2\beta}(x - \tilde{T}_{\mathrm{ir},i+3})^{\gamma_i}, \tag{33}$$

$$W_{1i}(x) = \tau_s'\left\{\frac{\omega_1\omega_2}{\omega_2 - \omega_1}[(x - \tilde{T}_{\mathrm{ir1}})^{1-\alpha_i} - (x - \tilde{T}_{\mathrm{ir2}})^{1-\alpha_i}] + \varphi_i\tau_s^{2\beta-1} \times \right.$$

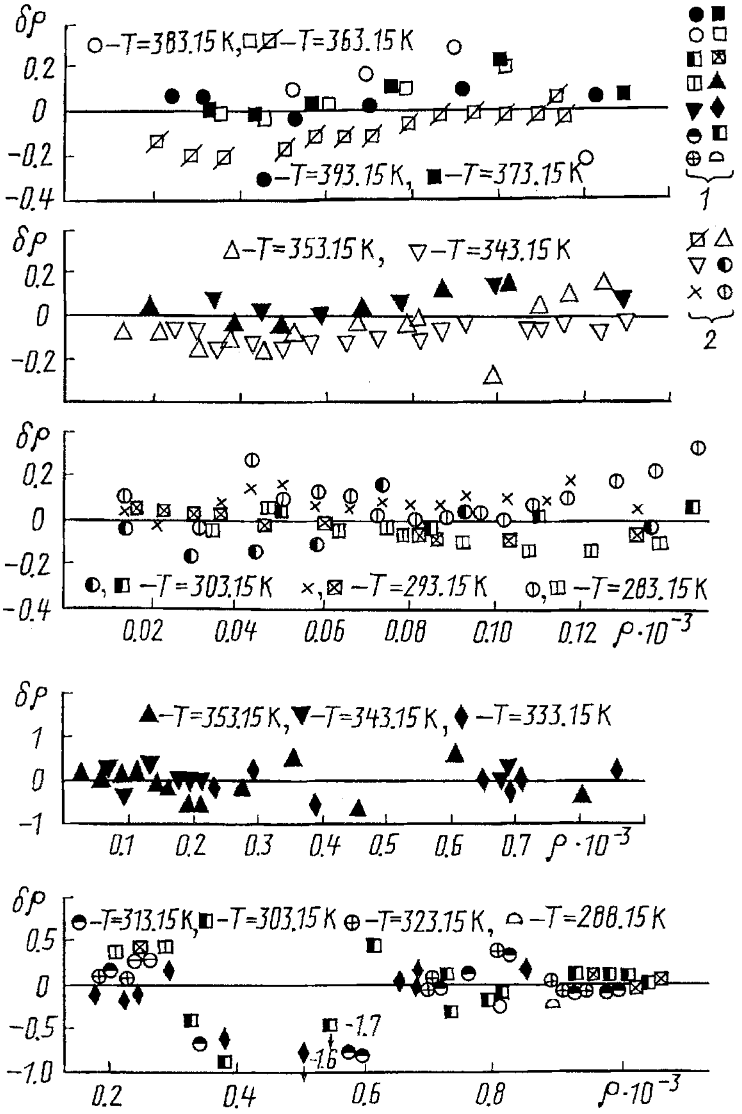

Fig. 2. Deviations of calculated values of ρ (%) from experimental data: 1) [17]; 2) [26].

$$\times (x - \tilde{T}_{\mathrm{ir},i+3})^{\gamma_i - 1} \left[\frac{2\beta}{\gamma_i} (x - \tilde{T}_{\mathrm{ir},i+3}) + \omega_{i+3}\,\tau_s \right] \Bigg\} . \tag{34}$$

It is easy to verify that all the conditions (2) – (15) follow from equation of state (31) – (34), i.e., unlike analytical equations of state the unified nonanalytical equation of state (31) – (34) qualitatively correctly describes specific features both of the regular part of a surface and of a wide neighborhood of the critical point. The thermodynamical functions obtained from (31) and (34) correctly take into account asymptotic, nonasymptotic, and asymmetric summands predicted by the current theory of critical phenomena.

Before analyzing the equation of state constructed, we must choose the values of the critical indices. In accordance with present-day estimates of these quantities [5, 9]

$$\alpha = 0.1085\,, \quad \beta = 0.325\,, \quad \delta = 4.82\,, \quad \gamma = 1.2185\,, \quad \Delta = 0.5\,. \tag{35}$$

$$\omega_1 = 3.113\,, \quad \omega_2 = 35.00\,, \quad \omega_3 = 9.123\,, \quad \omega_4 = 15.13\,. \tag{36}$$

In the next stage, we search for the coefficients E_i and B_i of (17) - (20), which specify the liquid-vapor phase equilibrium line of the substance under consideration. The present study deals with construction of the equation

TABLE 1. Coefficients a_{nm}, c_{kl}, and $b_{i\varepsilon}$

n	a_{nm}			
	$m=2$	$m=3$	$m=4$	$m=5$
1	426.51906550	−3530.2978757	8120.9053362	−6186.8449095
2	2918.4185626	−6727.9808967	4959.3154631	−912.57327599
3	−648.58647787	−510.68529952	2680.5398319	−2188.4443876
4	−1026.7139383	2644.3523328	−605.65066442	−689.71739283
l	c_{kl}			
	$k=1$	$k=2$	$k=3$	$k=4$
3	−1101.0550360	−695.65594795	9297.2150508	−19780.397292
4	1400.0735209	2508.3230139	−4623.8174346	670.19172963
5	−5732.9441810	1572.6413366	−5535.0792918	2478.7144228
6	10621.156646	2297.4107356	−121.28957268	2320.0225162
7	−6785.7408431	−5963.0560790	−1901.5404219	1053.6923243
l	$k=5$	$k=6$	$k=7$	$k=8$
3	20720.627525	−11653.973372	3336.4832699	−381.03878731
4	3913.3153517	−6102.6447215	3391.1175094	−603.04478925
5	5856.7373487	20.92523336	−129.81563584	−518.40659886
6	1535.4192794	−5558.4103294	−9288.1959633	4138.4015854
7	2602.8134722	450.98156039	−1327.6740868	5331.81297775
i	$b_{i\varepsilon}$			
	$\varepsilon=1$	$\varepsilon=2$	$\varepsilon=3$	$\varepsilon=4$
0	549.45266249	−2169.4282409	3869.7117809	3754.3408599
1	127.08675422	−415.19857035	338.22145326	−122.47884471
i	$\varepsilon=5$	$\varepsilon=6$	$\varepsilon=7$	$\varepsilon=8$
0	2029.9053063	−570.86242947	64.607376250	–
1	2.8384815283	2.5099679302	0.1862866138	–

of state of freezant $R23$. For it there are rather reliable data both for $P_s(T_s)$ [17] and for the densities of the saturated vapor and liquid $\rho^{\mathrm{v}}(T_s)$ and $\rho^{liq}(T_s)$ [18, 19]. Simultaneous processing of the indicated data array yielded the following values of the critical parameters and coefficients (17)–(20):

$$P_{\mathrm{cr}} = 4.795 \ \ \mathrm{MPa}\,, \quad T_{\mathrm{cr}} = 298.98 \ \ \mathrm{K}\,, \quad \rho_{\mathrm{cr}} = 525.0 \ \ \mathrm{kg/m}^3\,, \quad B_0 = 1.712984\,,$$

$$B_1 = 1.603758\,, \quad B_2 = 0.94044151\,, \quad B_3 = 0.5025530\,, \quad B_4 = -\,3.591770\,,$$

$$B_5 = 0.8250149\,, \quad B_6 = 3.691386\,, \quad B_7 = -\,2.491570\,,$$

$$E_{-1} = 20.81246\,, \quad E_1 = 13.39661\,, \quad E_2 = 28.15420\,, \quad E_3 = -\,13.45310\,,$$

$$E_4 = -\,15.22060\,, \quad E_5 = 43.61288\,. \tag{37}$$

Here, according to [20], $R = 118.744$ J /(kg·K) and $Z_{\mathrm{cr}} = 0.257262$. Figure 1 characterizes data on P_s, ρ^{v}, and ρ^{liq} reported in the literature and also shows analyzed quantities calculated by an analytical equation of state [20].

Having determined the equations describing the phase equilibrium line, we may begin to search for the coefficients a_{nm}, c_{kl}, and $b_{i\varepsilon}$ of equation of state (31). The results for pressure from [17, 21] and specific heat at constant volume from [2, 22] in the density range $0-2\rho_{\mathrm{cr}}$ were used as the array of experimental data. Solution

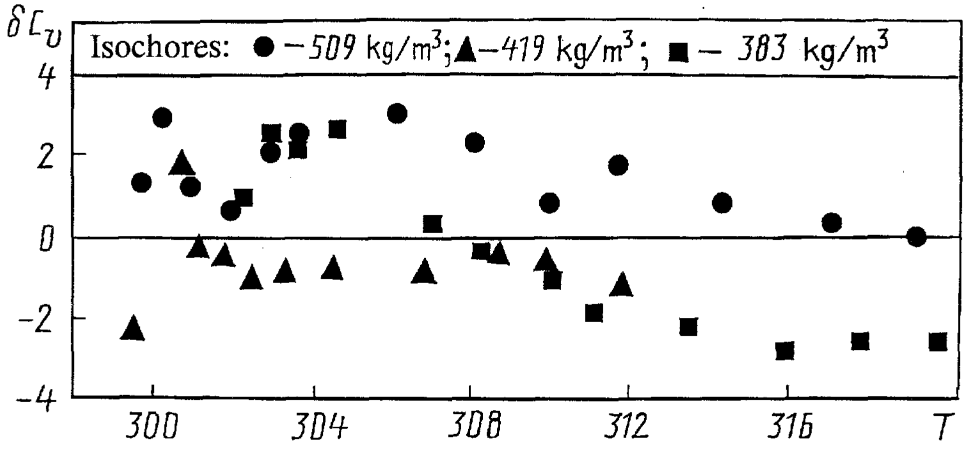

Fig. 3. Deviations of calculated values of C_v (%) from experimental data [2, 22].

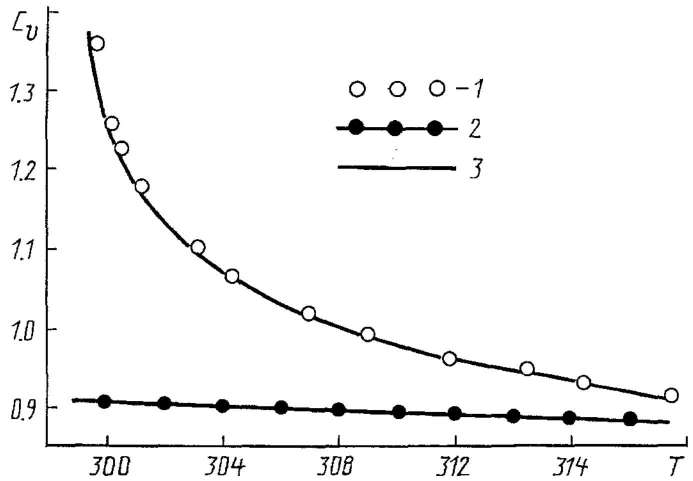

Fig. 4. Calculation of the specific heat at constant volume: 1) experimental data [2, 22]; 2) calculation by an analytical equation [20]; 3) by the suggested equation. C_v, kJ/(kg·K).

of an optimization problem produced the values of a_{nm}, c_{kl}, *and* $b_{i\varepsilon}$ cited in Table 1. Figures 2–4 show deviations of the experimental data from the calculated ones. The root mean square deviation of the pressure data [17, 21] is $\sigma_P = 0.21\%$, of the density data is $\sigma_\rho = 0.18\%$, and of the specific heat at constant volume [2, 22] is $\sigma_{c_v} = 1.6\%$. It is of interest that the constructed equation of state describes the experimental specific heat at constant pressure C_p [23, 24] and the Joule-Thompson effect δ_T [25] with errors of $\sigma_{C_p}=2.3\%$, $\sigma_{\delta_T} = 2.9\%$.

A comparison of the obtained results with analogous data calculated by an analytical equation of state of freezant *R*23 [20] allows the conclusion to be drawn that in the regular part of a surface both equations of state have approximately equal possibilities and, unlike the equation of state in [20], the suggested equation of state may be applied in a wide vicinity of the critical point.

REFERENCES

1. V. F. Lysenkov and E. S. Platunov, in: Surveys of Thermodynamical Properties of Substances [in Russian], No. 1, Inst. of High Temperatures, Acad. of Sciences of the USSR, Moscow (1984).
2. V. F. Lysenkov, Inzh.-Fiz. Zh., 47, No. 4, 602-608 (1984).
3. V. F. Lysenkov, N. V. Nimenskii, and E. S. Platunov, Teplofiz. Vys. Temp., 23, No. 1, 54-61 (1985).
4. A. D. Kozlov, V. F. Lysenkov, P. V. Popov, and V. A. Rykov, Inzh.-Fiz. Zh., 62, No. 6, 840-847 (1992).
5. V. F. Lysenkov and M. V. Yakovleva, Inzh.-Fiz. Zh., 65, No. 4, 1029 (1990).

6. V. V. Altunin, Thermophysical Properties of Carbon Dioxide [in Russian], Moscow (1975).
7. V. A. Rabinovich, A. A. Vasserman, B. A. Koval'chuk, and A. T. Berestov, in: Thermophysical Properties of Substances and Materials [in Russian], Issue 13, 24-39 (1979).
8. V. V. Sychev, A. A. Vasserman, A. D. Kozlov, et al., Thermodynamic Properties of Nitrogen [in Russian], Moscow (1977).
9. F. J. Wegner, Phys. Rev., **5**, No. 11, 4529-4536 (1977).
10. J. V. Sengers and J. M. H. Levelt Sengers, Int. J. Thermoph., **5**, No. 2, 195-208 (1984).
11. V. G. Martynets, E. V. Matizen, and A. G. Surtakov, Fiz. Nizk. Temp., **10**, No. 5, 503-509 (1984).
12. S. B. Kiselev, in: Surveys of Thermophysical Properties of Substances [in Russian], No. 2 (76), Inst. of High Temperatures, Acad. of Sciences of the USSR, Moscow (1989).
13. V. F. Lysenkov, P. V. Popov and M. V. Yakovleva, in: Thermophysical Properties of Substances and Materials [in Russian], Issue 31, 168-178 (1991).
14. V. F. Lysenkov and P. V. Popov, in: Surveys of Thermophysical Properties of Substances [in Russian], Inst. of High Temperatures, Acad. of Sciences of Russia, No. 1 (96), Moscow (1992).
15. V. F. Lysenkov and P. V. Popov, Inzh.-Fiz. Zh., **52**, No. 3, 501-503 (1991).
16. V. F. Lysenkov, P. V. Popov and V. H. Rykov, Tables of Recommended Reference Data [in Russian], GSSSD R 376-90, All-Union Research Center of Materials and Substances, Moscow, Deposited in VNIKI, November 24, 1990, No. 408 (1990).
17. D. S. Rasskazov, S. K. Petrov, and E. R. Ushmaikin, in: Properties of Substances, Cycles, and Processes [in Russian], Issue 234, 52-57, Moscow (1975).
18. A. M. Savandrin, T. Yu. Rasskazova, and Yu. R. Chashkin, in: Collected Papers on Chemistry and Chemical Technology. Thermodynamics of Organic Compounds [in Russian], Gor'kii, Issue 4 (43), 100-104 (1975).
19. Yu. G. El'kin, Candidate's Dissertation in Technical Sciences, Groznyi (1980).
20. V. V. Altumin, V. Z. Geller, E. K. Petrov, et al., Thermophysical Properties of Freons [in Russian], Vol. 1, Moscow (1980).
21. D. S. Rasskazov, E. K. Petrov, G. A. Spiridonov, et al., in: Thermophysical Properties of Substances and Materials [in Russian], Issue 8, 4-16 (1975).
22. N. V. Godinskaya and V. F. Lysenkov, Inzh.-Fiz. Zh., **60**, No. 6, 1037 (1991).
23. V. A. Gruzdev and A. I. Shumskaya, in: Thermophysical Properties of Substances and Materials [in Russian], Issue 8, 108-130 (1975).
24. O. P. Ponomareva and V. K. Romanov, in: Thermophysical Properties of Substances and Materials [in Russian], Issue 2, 18-23 (1989).
25. D. S. Rasskazov and L. A. Kryukov, in: Thermophysical Properties of Substances and Materials [in Russian], Issue 8, 84-99 (1975).
26. N. I. Timoshenko, E. P. Kholodov, and A. L. Yamkov, in: Thermophysical Properties of Substances and Materials [in Russian], Issue 8, 17-26 (1975).
27. W. Wagner, Kaltetechnik, Vol. 20, 238-240 (1968).
28. E. L. Elchardus and M. Maestre, La Revue Generate du Froid, 55, No. 8, 949-970 (1964).
29. W. Thomas and M. Zander, PTB-Mitt., 76, No. 5, 425-428 (1966).
30. Y. C. Hou and J. J. Martin, AIChE J., **1**, 125-129 (1959).