3. J. W. Tepper and F. Rohlich, Report AFML-TR-66-206. MSA Research Corp., Air Force Materials Laboratory, Ohio (1966), p. 67.
4. P. Y. Achener, A. R. Miller, and D. L. Fisher, Report AGN-8194, Aerojet-General Corp., San Ramon, Calif., Vol. 2 (1967), p. 29.
5. N. B. Vargaftik, L. D. Volyak, V. L. Stepanov, et al., Inzh.-Fiz. Zh., 39, No. 6, 986-992 (1980).
6. L. P. Fokin, V. V. Teryaev, Yu. S. Trelin, and A. G. Mozgovoi, "Review of the thermophysical properties of materials" (TFTs, Moscow), IVTAN, No. 4(42), pp. 3-43 (1983).
7. N. B. Vargaftik, L. D. Voljak, and V. G. Stepanov, Handbook of Thermodynamic and Transport Properties of Alkali Metals, Blackwell Scientific Publications, Oxford (1985), pp. 641-666.
8. L. D. Voljak, A. N. Nikitin, and V. G. Stepanov, Int. J. of Thermophysics, 8, No. 2, 239-246 (1987).
9. N. B. Vargaftik and V. S. Yargin, Inzh.-Fiz. Zh., 54, No. 1, 154-165 (1988).
10. L. D. Volyak, A. N. Nikitin, and V. G. Stepanov, Sb. Nauch. Tr. Mosk. Aviats. Inst., "Experimental and Theoretical Problems of Applied Physical Investigations," Moscow (1985), pp. 69-73.

THERMODYNAMIC PARAMETERS OF HYDROCARBONS IN THE CRITICAL RANGE.

1. n-OCTANE AND n-NONANE

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Scale equations of state have been derived for normal octane and nonane, which describe the thermal and caloric properties of those substances with an error close to the error of experiment.

Measurements have been made [1-3] on the P, ρ, T, and C_p dependence for normal octane and nonane in wide ranges around the critical points. In [1, 2], the P, ρ, and T data were recorded with a constant-volume piezometer relieved from pressure. The errors were 0.05-0.10% for pressure, 0.02-0.03 K, and 0.1% for the density (without allowance for the reference error). In [3], a flow adiabatic calorimeter was used to measure C_p. I estimate the errors to be 0.08-0.15% in pressure, 0.02-0.03 K, and 1.0-4.0% for the specific heat. The purity in both cases was better than 99.8%. In [4], the isochoric specific heat C_V was determined for those substances in the critical range, but those data are unreliable because the purity was not examined and no check was made on the onset of thermal decomposition. The [1-3] data have enabled me to construct equations of state in the critical region for n-octane and n-nonane. I used a scale equation of state [5], which in parametric form is

$$\Delta\mu = ar^{\beta\delta}\theta(1-\theta^2) + cr^{\beta\delta+\Delta}\theta + r^{2\nu+2\beta-1}[d(1+e_1b^4\theta^4) + fb^2\theta^2(1+e_2b^2\theta^2)], \tag{1}$$

$$\tau = r(1-b^2\theta^2), \tag{2}$$

$$\Delta\rho = kr^{\beta}\theta - B_3\tau. \tag{3}$$

Here $\Delta\mu = [\mu(\rho, T) - M_0(\tau)]\rho_c/P_c$, $\tau = T/T_c - 1$, and $\Delta\rho = \rho/\rho_c - 1$ are correspondingly the dimensionless chemical potential, the temperature, and the density; r and θ are polar coordinates characterizing the point on the thermodynamic surface, and in particular, r defines the distance of that point from the critical one and θ the angle of rotation.

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TABLE 1. Coefficients in the Scale Equation of State for n-Octane and n-Nonane

n-Octane	n-Nonane
Critical parameters	
$T_c = 568{,}60$ K	$T_c = 594{,}4$ K
$P_c = 2{,}480$ MPa	$P_c = 2{,}2954$ MPa
$\rho_c = 234{,}0$ kg/m^3	$\rho_c = 234{,}0$ kg/m^3
Thermal coefficients	
$a = 29{,}110$	$a = 29{,}540$
$c = -1{,}6547$	$c = -28{,}539$
$d = -28{,}287$	$d = 0{,}0$
$f = 42{,}079$	$f = 0{,}0$
$f_1 = -8{,}3450$	$f_1 = -8{,}9676$
$f_2 = 33{,}758$	$f_2 = 27{,}091$
$f_3 = -747{,}11$	$f_3 = 0{,}0$
$f_4 = 0{,}0$	$f_4 = 0{,}0$
$k = 1{,}4140$	$k = 1{,}0224$
$B_3 = 0{,}0$	$B_3 = 0{,}0$
Caloric coefficients	
$m_2 = -65{,}909$	$m_2 = -44{,}489$
$m_3 = 169{,}37$	$m_3 = -405{,}59$
$m_4 = 9830{,}1$	$m_4 = 0{,}0$

From (1)-(3) we get an expression for the free energy, which on differentiation gives expressions for all the thermodynamic quantities (see [5, 6] for details). The formulas for the pressure and specific heat are

$$P = P_c\,[(\Delta\rho + 1)\,\Delta\mu\,(r,\ \theta) - \Psi\,(r,\ \theta) - \Phi_0\,(\tau)], \qquad (4)$$

$$C_{\tau} = -\frac{P_c T}{T_c^2\,\rho}\left[\left(\frac{\partial^2\Psi}{\partial\tau^2}\right)_{\Delta\rho} + 2B_3\left(\frac{\partial\Delta\mu}{\partial\tau}\right)_{\Delta\rho} + B_3^2\left(\frac{\partial\Delta\mu}{\partial\Delta\rho}\right)_{\tau} + \rho/\rho_c M_0''(\tau) + \Phi_0''(\tau)\right], \qquad (5)$$

$$C_p = C_v + \frac{T}{\rho}K_T\left(\frac{\partial P}{\partial T}\right)_{\rho}^{2}. \qquad (6)$$

All the quantities in (1)-(3) and (4)-(6) are given in the Appendix.

I initially used the [1, 2] data to construct the scale equation of state, with (4) fitted to them. For n-octane, I took the data for the 166.6; 193.5; 225.0; 233.3; 256.6; 295.8; 330.4 kg/m^3 isochores at 568.65-585.0 K, and for n-nonane, the data for the 592.15; 593.15; 594.57; 596.00; 596.15; 623.15 K isotherms at densities of 142.45-323.56 kg/m^3. During the fitting, I refined the critical parameters for n-octane and n-nonane on the basis of the best description of the entire data set for P, ρ, and T. The initial values of the critical parameters P_c, T_c, ρ_c were taken from [1, 2], which were then varied, particularly the critical temperature, which was not measured in [1, 2].

That processing gave the thermal coefficients in (4) and the critical parameters, which are given in Table 1. The standard deviation in describing the pressure for n-octane was 0.13%, and for n-nonane 0.28%.

Table 1 shows that f_4 for n-octane and f_3 and f_4 for n-nonane are zero because my data did not cover a wide temperature range and those coefficients lack significance in (4). One reason for the restricted temperature range is that n-octane and n-nonane begin to decompose at about 623.15 K.

Figure 1 shows the deviations in the calculated pressures from the observed ones, which are not systematic.

To derive a scale equation of state for all the thermodynamic quantities, one needs data on the specific heat or the speed of sound. I used the measured C_p [3] for the near-critical 2.70, 3.00, and 3.50 MPa isobars for n-octane and 2.50 and 3.00 MPa for n-nonane. I fitted (6) to the C_p data, in which all the thermal coefficients previously determined were fixed. Only the caloric coefficients m_i were stepped in the approximation (see the

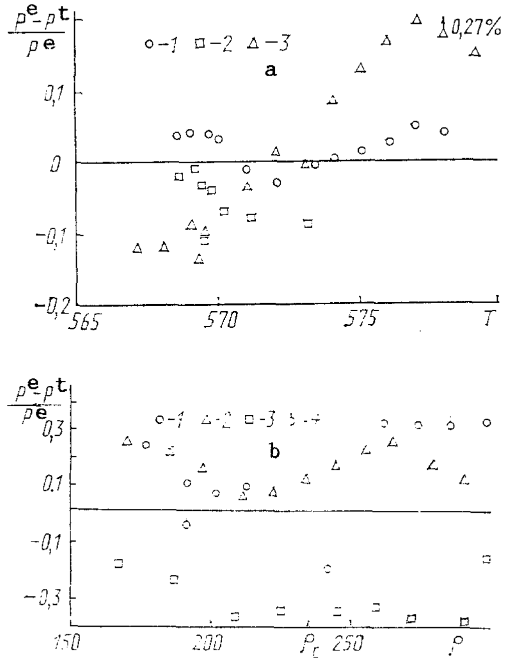

Fig. 1. Deviations in observed pressures: a) n-octane [1] from the values calculated from (4) on certain isochores: 1) ρ = 167; 2) 233; 3) 330 kg/m³; b) n-nonane [2] from the values calculated from (4) on certain isotherms" 1) T = 594.57; 2) 596; 3) 591.15; 4) 623.15 K: $\Delta P = (P^e - P^t)/P^e$, %; T, K; ρ, kg/m³.

Appendix). Table 1 gives these m_i. Table 2 gives the errors in describing the observed isobars via (6). For n-nonane, Table 2 has the 2.500 and 3.00 MPa isobars replaced by certain others, since when I processed the C_p data for n-nonane I found that the fitting was substantially improved if the pressures on the isobars were increased by 0.009 MPa. The error in describing the C_p was then reduced from 13.93 to 8.59%. That pressure correction appears possible because it does not exceed the overall errors in the P, ρ, T, and C_p data. Figure 2 shows the calculated maxima in the specific heats for n-octane and n-nonane. Figure 2b shows that the specific heat of n-nonane begins to rise above 618.0 K on the 3.009 MPa isobar, which is physically incorrect and indicates that the region of action for the scale equation for n-nonane is bounded by 618.0 K. That result is possible because all the major coefficients in the scale equation for n-nonane were derived from P, ρ, and T data in which the maximum temperature was 585.0 K.

In calculations on C_p (and correspondingly during fitting) from (6), it is necessary to know ρ. This was calculated from (4) for each observed point in the C_p, P, and T data for the corresponding P and T. As the C_p data on the 3.009 MPa isobar lie above 610.0 K, the calculated densities for those temperatures are extrapolated, and probably 618.0 K is the limit to which (4) can be extrapolated.

The [4] data on the isochoric specific heats of the normal alkanes, including n-octane and n-nonane, are unreliable, but nevertheless, we compared the values from the scale equations derived from (5) with the [4] C_v data. For n-octane, we used those data on the 322.5, 303.03, 285.71, 250.0, 234.9, 222.2, 200.0, 181.82, 166.67, 156.25, 147.06, and 142.86 kg/m³ isochores at 573.15-603.15 K, and for n-nonane, the [4] data on the 290.20, 270.90, 236.20, 222.37, 213.63, 206.19, and 170.94 kg/m³ isochores at 596.15-623.15 K. The standard deviations in the [4] data from the calculated ones were 65.88% for n-octane and 35.38% for n-nonane.

The deviations vary smoothly with temperature and are much larger than the error of experiment [4]. This again shows that the [3] C_p are not matched to the [4] C_v ones.

On the whole, these scale equations describe the thermal and caloric parameters of n-octane and n-nonane with an error satisfactory for engineering purposes in the critical range.

I am indebted to A. A. Gerasimov and M. A. Kuznetsov for providing their unpublished data on the isobaric specific heats of n-octane and n-nonane.

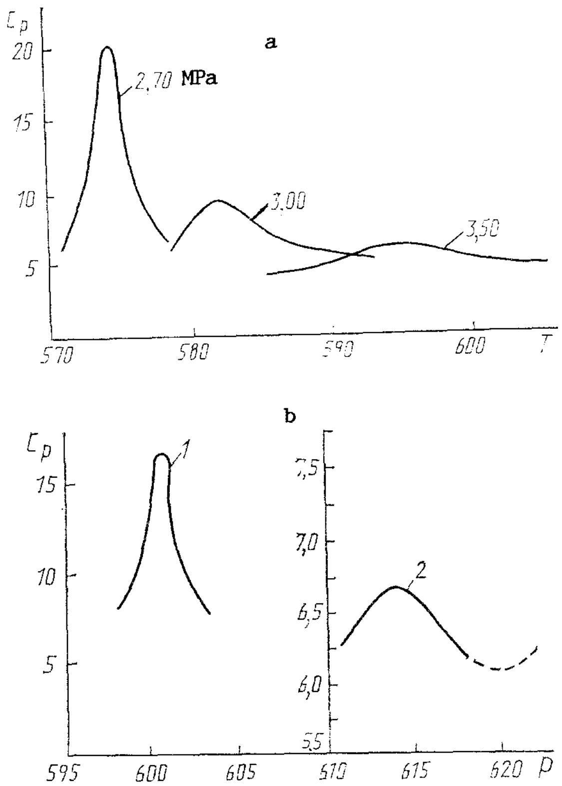

Fig. 2. Calculated isobaric specific heats: a) n-octane; b) n-nonane: 1) p = 2.509 MPa; 2) 3.009 MPa. C_p in kJ/kg·K, P in MPa.

TABLE 2. Errors in Describing the Isobaric Specific Heats of n-Octane and n-Nonane by Means of Scale Equations

n-Octane			n-Nonane		
Isobar, MPa	σ, %	Δc_p^{max*}, %	Isobar, MPa	σ, %	Δc_p^{max*}, %
2,70	4,35	9,87	2,509	11,86	20,45
3,00	5,05	10,23	3,009	2,51	3,87
3,50	6,30	16,92			
Over-all error	6,64%		Over-all error	8,59%	

$*\Delta C_p = (C_p^e - C_p^t/C_p^e) \cdot 100$.

APPENDIX

α, β, δ, Δ, and γ are universal critical parameters. Theoretical estimates [7] give α = 0.11; β = 0.325; Δ = 0.50, while δ = 4.815 and γ = 1.24 were calculated from

$$\alpha + 2\beta + \gamma = 2; \quad \beta(\delta - 1) = \gamma; \tag{A.1}$$

$$b^2 = (\gamma - 3\beta)/\gamma(1 - 2\beta); \tag{A.2}$$

$$e = 2\gamma + 2\beta - 1; \quad e_1 = \frac{(5 - 2e)(e - \beta)(3 - 2e)}{3(5\beta - e)};$$

$$e_2 = \frac{(5 - 2e)(e - 3\beta)}{3(5\beta - e)}; \tag{A.3}$$

with k, B_3, a, c, d, and f dimensionless nonuniversal constants to be determined by experiment.

The free energy is

$$F = \frac{P_c}{\rho}\left[\Psi(r,\ \theta) + (\Delta\rho + 1)\,M_0(\tau) + \Phi_0(\tau)\right], \tag{A.4}$$

in which $\Psi(r, \theta) = \Psi_{LM}(r, \theta) + \Psi_{NA}(r, \theta) + \Psi_{AS}(r, \theta)$ is the singular part of the free energy and

$$\Psi_{LM} = \frac{1}{2}\,\frac{akr^{2-\alpha}}{b^4}\left[\frac{2\beta\,(b^2 - 1)}{2-\alpha} + \frac{2\beta\,(2\gamma - 1)}{\gamma\,(1-\alpha)}\,(1 - b^2\theta^2) + \right.$$

$$\left. + \frac{(2\beta - 1)\,(1 - b^2\theta^2)^2}{\alpha}\right]; \tag{A.5}$$

$$\Psi_{AS} = kr^{2\gamma+3\beta-1}\theta\left\{d + \frac{1}{3}\,[f - 2d\,(e-\beta)]\,b^2\theta^2 + \right.$$

$$\left. + \frac{1-2\beta}{5-2e}\,[de_1 + fe_2]\,b^4\theta^4\right\}; \tag{A.6}$$

$$\Psi_{NA} = \frac{1}{2}\,\frac{ckr^{2-\alpha+\Delta}}{b^2\,(1-\alpha+\Delta)}\left[\frac{\gamma+\Delta}{2-\alpha+\Delta} - (1-2\beta)\,b^2\theta^2\right]; \tag{A.7}$$

with $\Phi_0(\tau)$ and $M_0(\tau)$ analytic functions of temperature,

$$\Phi_0(\tau) = -1 + \sum_{i=1}^{4} f_i\tau^i; \tag{A.8}$$

$$M_0(\tau) = \sum_{i=0}^{4} m_i\tau^i; \tag{A.9}$$

$$K_T = \frac{\rho_c^2}{P_c\rho^2}\left(\frac{\partial\Delta\mu}{\partial\Delta\rho}\right)_\tau^{-1}; \tag{A.10}$$

K_T being the isothermal compressibility, and

$$s = -\frac{P_c}{\rho_c T_c}\left[\left(\frac{\partial\Psi}{\partial\tau}\right)_{\Delta\rho} + M_0'(\tau) + \Phi_0'(\tau)\right]; \tag{A.11}$$

$$h = \frac{P_c}{\rho_c}\,[\Delta\mu\,(r,\ \theta) + M_0(\tau)] + Ts. \tag{A.12}$$

NOTATION

P pressure; T temperature; ρ density; C_p isobaric specific heat; C_v isochoric specific heat; s entropy; h enthalpy. Subscripts: c critical, e experimental, t theoretical.

LITERATURE CITED

1. A. G. Badalyan, The Density and Viscosity of n-Octane from the Triple Point up to Pyrolysis Temperatures: Ph.D. Thesis [in Russian], Groznyi (1987).
2. S. A. Topchiev and D. S. Kurumov, Thermophysical Parameters of Pure Substances and Mixtures [in Russian], Makhachkala (1990), pp. 35-38.
3. M. A. Kuznetsov, The Caloric Properties of Normal Alkanes over a Wide Range in State Parameters: Ph.D. Thesis [in Russian], Groznyi (1988).
4. Kh. I. Amirkhanov, B. G. Alibekov, D. I. Vikhrov, and V. A. Mirskaya, The Isochoric Specific Heat and Other Caloric Parameters for Normal Hydrocarbons [in Russian], Makhachkala (1981).
5. S. B. Kiselev, Teplofiz. Vysok. Temp., 24, No. 3, 500-509 (1986).
6. I. G. Kostyukova, The Equation of State and Thermophysical-Parameter Calculation for a Wide Range Around the Critical Point: Ph.D. Thesis [in Russian], Moscow (1987).
7. M. A. Anisimov, Critical Phenomena in Liquids and Crystals [in Russian], Moscow (1987).