2. T. A. Apaev, S. I. Lipovetskii, and A. A. Gylmanov, "Some thermodynamic properties of liquid isoamyl alcohol over a wide range of state parameters," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 12, 89-100 (1977).

EXPERIMENTAL INVESTIGATION AND DEVELOPMENT OF A METHOD FOR COMPUTING THE THERMOPHYSICAL PROPERTIES OF HYDROCARBONS AND PETROLEUM PRODUCTS

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The results of comprehensive experimental investigations of the thermophysical properties of n-hexane and cyclohexane and the thermoconductivity of liquid petroleum products are presented.

The thermophysical properties (specific volumes v, isobaric heat capacity C_p, and dynamic viscosity η) of n-hexane and cyclohexane were studied from the triple point to their transition points, including the liquid, vapor, two phase, critical, and supercritical regions. The C_6H_{14} specimen, after additional purification, contained 99.93% of the principal component (mixture: 2- and 3-methylpentane 0.047%, methylcyclohexane 0.023%); the C_6H_{12} specimen contained 99.90% of the principal component (mixture: cycloparafin and its derivatives 0.06%, aromatic hydrocarbons 0.04%). We monitored the purity of the specimens studied by periodic sampling for different values of the parameters p and t while making sample tests followed by a determination of their relative density ρ_4^{20} and index of refraction n_d^{20} and analysis on the Tsvet-4.69 and Khrom-4 chromatographs.

The upper temperature limits for measurements of the properties of n-hexane (350°C) and cyclohexane (425°C) are determined by the thermostability of these substances in piezometers, calorimeters, and viscosimeters, made of chrome-nickel steels. The parameters (p and t) corresponding to the transition points of hydrocarbons were established in experiments measuring v. For C_6H_{14}, beginning with 325°C, and for C_6H_{12} beginning with 375°C, samples were extracted at different pressures in the piezometers, which were subjected to special physicochemical tests, including fractional distillation in a capillary column ($d = 0.25$ mm, $l = 50$ mm) followed by chromatographic analysis. It was established that in C_6H_{14} there are no transitions for $t \leqslant 350$°C and in C_6H_{12}, for $t \leqslant 425$°C and $p > 11$ MPa.

In view of the fact that the measurements of v, C_p, and η for cyclohexane at low temperatures and high pressures were carried out near its melting curve, special tests were made in order to determine the melting pressure p_{melt} in the temperature range 9.9-42.9°C. p_{melt} was measured with the use of the falling body method [1, 2] and the capillary method [3], used in viscosimetry. The melting curve was approached from the solid phase side. The values of p_{melt}, obtained with two experiments, agree within 0.2-0.3%. The experimental values of p_{melt} for cyclohexane were approximated by the equation

$$p_{\text{melt}} = -10.8918 + 1.65297t + 0.0037149t^2. \tag{1}$$

The mean-square deviation of the computed values of p_{melt} from the experimental values constitutes 0.15%, and the maximum error in determining p_{melt} is 3%. Equation (1) encompasses the temperature range from 6.554 to 43°C. The value $p_{\text{melt}} = 0.1013$ MPa at $t = 6.554$°C was taken from the data in [4].

The saturated vapor pressure for C_6H_{14} and C_6H_{12} was studied by the piezometer method at constant volume [5] in the temperature ranges 100-234.7°C and 110-281°C, in which there is

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considerable disagreement in the data of different workers. Two series of measurements were performed for each substance (along isochores and isotherms). For $\tau > 0.92$ ($\tau = T/T_{cr}$) p_{s_i} were measured for different times p_s in the experiments along isochores for fixed temperatures. Then, in order to eliminate errors in determining θ_i, due to the fact that an equilibrium state may not have been reached, the limiting value of p_s, which was taken as the saturation pressure at a given temperature, was determined by graphical extrapolation in the coordinates $p_s - 1/\theta$ to the value $1/\theta = 0$.

As a result of simultaneous analysis of the results of this work, as well as more reliable data of other researchers [4, 6], interpolation equations were obtained for calculating the saturated vapor pressures:

n-hexane

$$\ln p_s = -10.23965\,\frac{T_{\mathrm{cr}}}{T} + 20.03273 - 14.45616\,\frac{T}{T_{\mathrm{cr}}} + 5.78056\left(\frac{T}{T_{\mathrm{cr}}}\right)^2; \tag{2}$$

cyclohexane

$$\begin{aligned}\lg p_s = {} & 0.644304\,\lg(T - 273.15) + 3.275631\,(T - 273.15)^{-1} - 11.274370 + \\ & + 4.655635\cdot 10^{-2}T - 7.5738335\cdot 10^{-5}T^2 + 4.55841\cdot 10^{-8}T^3,\end{aligned} \tag{3}$$

where p_s is the saturated vapor pressure, MPa; T, °K.

The average errors in calculating p_s from (2) and (3) in the temperature ranges 95.32-234.7°C and 20-281°C constitute 0.1%, with the exception of regions near the triple point of n-hexane, where the computational errors attain 1.5%.

The specific volumes of C_6H_{14} and C_6H_{12} were measured by the unloaded spherical constant volume piezometer method, developed in the All-Union Heat Engineering Institute (AHI). The design of the experimental setup and the technique for the studies are described in [5, 7]. The measurements of v for n-hexane were performed in the temperature range 50-375°C and pressure range 0.1-150 MPa, while for cyclohexane, the measurements were carried out in the range 10-450°C and 0.1-85 MPa. More than 1500 experimental values of the specific volumes were obtained [8-12]. The experimental magnitudes were measured with the following errors: temperature 0.006-0.03°C, pressure 0.02-0.05%, and specific volumes 0.05-0.07% (liquid phase) and 0.1-0.2% (vapor phase).

In order to provide an analytic description of the experimental data, we checked the following equations of state for liquids: Tait, Lennard-Jones and Devonshire, Akhundov, Byron-Manedov, et al. The best results were obtained for the equations proposed by Akhundov and his co-workers [13]. As a result of analyzing the experimental data for n-hexane, we obtained the equation

$$pv^2 = K_1(T) + L_1(T)/v^6, \tag{4}$$

where

$$K_1(T) = \sum_{i=0}^{5} k_i\,(T/100)^i; \quad L_1(T) = \sum_{j=0}^{5} l_j\,(T/100)^j;$$

$$k_0 = -1246.5786; \quad k_3 = -62.3731; \quad l_0 = 14058.506; \quad l_3 = -2610.768;$$

$$k_1 = 760.1567; \quad k_4 = -7.8334; \quad l_1 = -17122.152; \quad l_4 = 344.1504;$$

$$k_2 = -267.9361; \quad k_5 = 0.3995; \quad l_2 = 9685.21; \quad l_5 = -17.5632.$$

For cyclohexane

$$pv^2 = K_2(T) + L_2(T)/v^7, \tag{5}$$

where

$$K_2(T) = -\frac{254,2378}{T - 273,15} - \sum_{i=0}^{3} k_i T^i; \quad L_2(T) = \sum_{j=0}^{3} l_j T^j;$$

$$k_0 = -698.15712; \quad k_2 = 0.2736962\cdot 10^{-2}; \quad l_0 = 928.1661; \quad l_2 = 1.583636\cdot 10^{-3};$$

$$k_1 = 2{,}3549754;\; k_3 = 1{,}48624\cdot 10^{-6};\; l_1 = 0{,}48777;\; l_3 = 1{,}239365\cdot 10^{-5}.$$

The dimensions are MPa for p, 10^{-3} m^3/kg for v, and K for T.

The error in calculating the specific volumes of n-hexane from (4) in the temperature range 50-350°C and $v < 0.47\, v_{cr}$ does not exceed 0.15%. Equation (5) describes the experimental data for cyclohexane in the temperature range 25-425°C and $v < 0.54\, v_{cr}$ with an error not exceeding 0.05%.

Equations (4) and (5) describe satisfactorily the variation in the isobaric heat capacity of C_6H_{14} and C_6H_{12} as a function of pressure. The deviations of the computed values of C_p from the experimental values do not exceed 0.5%.

In order to explain the P—v—T data for C_6H_{14} and C_6H_{12} in the vapor phase, the virial form of the equation of state was used. The experimental data obtained permitted separating out the second and third virial coefficients. The correcting temperature function D (fourth virial coefficient) was also computed for n-hexane. The virial coefficients were determined by Keis's grahical method and by the Moscow Energy Institute (MEI) method [14].

The virial equations adopted have the following form:

for n-hexane

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}\,; \tag{6}$$

for cyclohexane

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2}\,. \tag{7}$$

The analysis of data on the virial coefficients resulted in the following equations:

for n-hexane

$$B = \sum_{i=0}^{5} b_i \tau^i,\quad C = \sum_{i=0}^{5} c_i \tau^i,\quad D = \sum_{i=0}^{4} d_i \tau^i, \tag{8}$$

where

$$\begin{array}{lll}
b_0 = -433{,}74; & c_0 = 6250.18; & d_0 = 8912.06;\\
b_1 = 1870.07; & c_1 = -33319.55; & d_1 = -3463.15;\\
b_2 = -3392{,}22; & c_2 = 70074{,}90; & d_2 = 49942.13;\\
b_3 = 3153{,}16; & c_3 = -72598.01; & d_3 = -31739.05;\\
b_4 = -1484.36; & c_4 = 37094.54; & d_4 = 7507.32;\\
b_5 = 281.41; & c_5 = -7489.23; &
\end{array}$$

for cyclohexane

$$B = b \lg t + \sum_{i=-1}^{2} b_i t^i\,, \tag{9}$$

$$C = c_1 + \{c_2 \cos[c_3(t + c_4)] + c_5 \sin[c_3(t + c_4)]\} \exp[c_6(t + c_4)], \tag{10}$$

where

$$b = 12{,}23858;\; b_1 = 0{,}013202;\; c_1 = 5{,}3817;\; c_4 = -176{,}600;$$

$$b_{-1} = -95{,}94646;\; b_2 = -0{,}23339\cdot 10^{-4};\; c_2 = -13{,}3817;\; c_5 = 28{,}3769;$$

$$b_0 = -36{,}07533;\qquad c_3 = 0{,}0143272;\; c_6 = -0{,}025665.$$

Equation (6) describes the experimental data on v for n-hexane in the vapor phase (for $v > v_{cr}$) with an average error ±0.14%, and Eq. (7) describes the experimental data on v for cyclohexane in the temperature range 160-425°C (for $v > 2v_{cr}$) with average error ±0.15%. The deviations of the values of C_p computed using (6) and (7) from the experimental values do not exceed 1.5%.

For n-hexane, analysis of the experimental P—v—T data in the liquid and vapor phases using the MEI methods [14] yielded a single equation of state:

TABLE 1. Values of the Coefficients $\{b_{ij}\}$ for the Equation of State (11)

i	0	1	3	3
0	—3,1405882	—7,5742526	1,8126773	—0,0809262
1	8,5208681	28,894534	168,05948	387,52014
2	—15,077490	—186,8287	—817,38044	—1408,3184
3	10,365252	—734,52141	—4983,0247	—9491,2784
4	272,30117	4977,7671	37380,440	54523,489
5	506,08372	3454,8027	—18211,685	—34142,572
6	—1921,9996	—67064,398	—446671,09	—265972,58
7	—3643,9528	156091,04	1562659,4	580288,83
8	19895,918	—140944,31	—2154046,6	—341936,47
9	—20026,333	44709,446	1102957,8	—18705,192

$$Z = 1 + \rho \sum_{i=0}^{9} \sum_{j=0}^{3} b_{ij} (\rho - \rho_{cr})^i \left(\frac{1}{\tau} - 1 \right)^j , \tag{11}$$

where $Z = p/\rho RT$ is the compressibility coefficient; $\tau = T/T_{cr}$, reduced temperature; ρ_{cr}, critical density.

The value $\rho_{cr} = 233.6$ kg/m^3 is obtained from the results of the present investigation.

The matrix of coefficients $\{b_{ij}\}$ is presented in Table 1. The specific volumes in the vicinity of the liquid state are computed from (11) with an average error of 0.07% and in the gas phase for t = 234.7-350°C with an error of 0.15%. For $t < t_{cr}$, the errors in computing v increase and attain 0.8%.

Detailed tables of the specific volumes of n-hexane and cyclohexane, as well as the values of p_s, v', v'', and the heat of vaporization, were computed from the proposed equations (1)-(11) starting with the triple point to the transition points.

The isobaric heat capacity of n-hexane and cyclohexane was studied using the method of flow-through adiabatic calorimetry with a closed circulation loop and with a calorimetric measurement of the flow rate [15, 16]. In reproducing the well-known technique [15], the construction of the separate units involved changes related to the specific properties of the substances being examined (the construction of the gear-type pump for creating a constant flow rate was modified; the reducer of the pump gear was improved so as to stabilize the flow rate of the substance being studied through the calorimeter and to decrease the fluctuations in pressure; a system was created for heating the supply lines in order to avoid the transition of cyclohexane into the solid phase at high pressures; better insulation was used for the thermoelectrodes of the platinum-gold thermocouples on the principal calorimeter).

The isobaric heat capacity of C_6H_{14} was measured in the temperature range 20-350°C and pressures up to 60 MPa, C_6H_{12} at 20-400°C and 0.5-50 MPa [16-18]. The experiments were mainly carried out along isotherms with equal pressures. Near the saturation line, as well as near the maxima in the heat capacity, the measurements were carried out along the isobars with small steps in temperature. The steps in pressure and temperature were determined according to the change in the C_p-P-T surface for given state parameters. The smallest magnitude of the pressure step was 0.5 MPa. For subcritical pressures, the heat capacity of C_6H_{14} was measured for pressures 0.5, 1.0, 1.5, 2.0, 2.5, 2.7, 2.8, 2.9, and 3.0 MPa, and for C_6H_{12} for pressures 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 MPa.

In order to separate out values of C_p' and C_p'', the saturation curve was approached from the liquid side as well as from the vapor side. In this case, the temperature of the experiment differed from the saturation temperature by 0.7-2°C. The values of C_p' and C_p'' for n-hexane and cyclohexane were determined graphically by extrapolating the isobars to the saturation temperature. For n-hexane, the data on C_p' obtained in the temperature range 20-232°C were analyzed simultaneously with the more precise data [19] in the low temperature region. As a result, an interpolation equation was obtained, which described C_p' from the triple point to $\tau = 0.995$ with a standard deviation of 0.32%:

$$\frac{C_p'}{T} = 7.5137 - 2.78802 \frac{T_{cr} - T}{100} + 2.94048 \left(\frac{T_{cr} - T}{100} \right)^2 -$$

$$-1.16467\left(\frac{T_{cr}-T}{100}\right)^{3}+0.190097\left(\frac{T_{cr}-T}{100}\right)^{4}+0.24136\left(\frac{T_{cr}-T}{100}\right)^{-1,206}, \tag{12}$$

where C_p', J/kg·K; T_{cr} = 507.85 K.

In the vapor phase, C_p'' of n-hexane was determined from the normal boiling temperature up to 231°C and approximated by Eq. (13) with a standard deviation of 0.48%:

$$\frac{C_p''}{T}=4.67467+0.2841\cdot\frac{T_{cr}-T}{100}+0.737207\left(\frac{T_{cr}-T}{100}\right)^{1.091} \tag{13}$$

Detailed tables of the heat capacity for equal values of temperature and pressure were constructed from the results of the experimental investigation of C_p for n-hexane and cyclohexane. A graphical analytical method was used here. Sections of the thermodynamic $C_p(p, t)$ surface were constructed with a temperature step of 10°C and a pressure step of 0.5 MPa: p = const, t = const, and C_p = const. For regions where graphical interpolation is reliable, smooth values of C_p were obtained. In the region of maxima in C_p, smoothing and interpretation were carried out by the method proposed in [15]. The experimentally measured isobars in the $C_p(p, t)$-surface were constructed first. Then, using Timrot's rectilinear diameter method, the magnitudes of $C^p_{p,m}$ and the position of the t^p_m maxima were determined. Then, the isobars $C_p/C^p_{p,m} - (t - t^p_m)$ were constructed from the experimental data, and the coordinates $p - (t - t^p_m)$ for the $C_p/C^p_{p,m}$ = const diagram were obtained according to them. $C_p/C^p_{p,m}$ curves with a small curvature have a single common point and allow for reliable interpolation of the experimental data near the maxima.

In order to construct detailed tables of the heat capacity near the maxima, it is necessary to have an analytic equation that permits calculating the magnitude of $(C^p_{p,m})$ and the position of the (t^p_m) maxima. Due to the limited size of the region in which the relations proposed in [15, 20, 21] can be used, the magnitudes and positions of the maxima in the pressure range 3.3-9 MPa for C_6H_{14} and 4.5-10 MPa for C_6H_{12} were approximated by the following empirical equations:

$$\frac{C^p_{p,m}}{T^p_m}=\sum_{i=0}^{2}a_i\left(\frac{T^p_m-T_{cr}}{100}\right)^i+a_3\left(\frac{T^p_m-T_{cr}}{100}\right)^n, \tag{14}$$

$$p_m-p_{cr}=\sum_{j=1}^{4}b_j\left(\frac{T^p_m-T_{cr}}{100}\right)^j \tag{15}$$

where (C_p, J/kg·K) for n-hexane

$$a_0=3,36044;\quad a_3=1.9263;\quad b_1=4.432207;\quad b_3=4.572416;\quad a_1=1,38181;$$

$$n=-1,025;\quad b_2=1,32616;\quad b_4=-3.98566;\quad a_2=-0,5068;$$

for cyclohexane

$$a_0=1,570908;\ a_3=2,62076;\ b_1=5,456341;\ b_3=6,18454;\ a_1=2,453624;$$

$$n=-0,8870;\ b_2=0,20997;\ b_4=-4,825;\ a_2=-0,75169.$$

The mean-square error in determining $C^p_{p,m}$ from (14) is 0.38% and the maximum error is 0.56%. The mean error in computing the position of the maxima on the isobars from (15) is 0.05°C and the maximum error is 0.13°C.

The critical specific volumes v_{cr} for C_6H_{14} and C_6H_{12} were determined from the experimental C_p data in the supercritical region by linear extrapolation of the function $(C_{p,m} - C_p^o)^{-1} = f(v)$ to the critical point at which $(C_{p,m} - C_p^o)^{-1} = 0$. These values agree within 1% with the values found from the p–v–T data using the phenomenological Planck–Gibbs rule.

The enthalpy and the entropy of C_6H_{14} and C_6H_{12} were determined from detailed tables of the isobaric heat capacity by graphical integration and tables were constructed for all values of state parameters studied. In doing so, the crystalline state was taken at 0°K.

The dynamic coefficient of viscosity for n-hexane and cyclohexane was studied by the capillary method using the Golubev viscosimeter design [22] (the IV variant). The experimental setup and the technique for doing the analysis are presented in [3]. Analysis of the

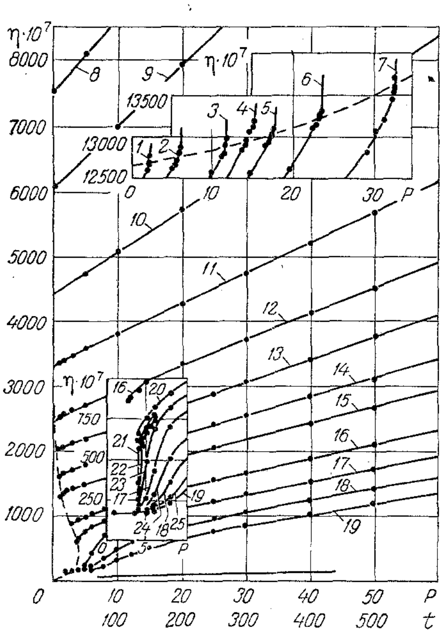

Fig. 1

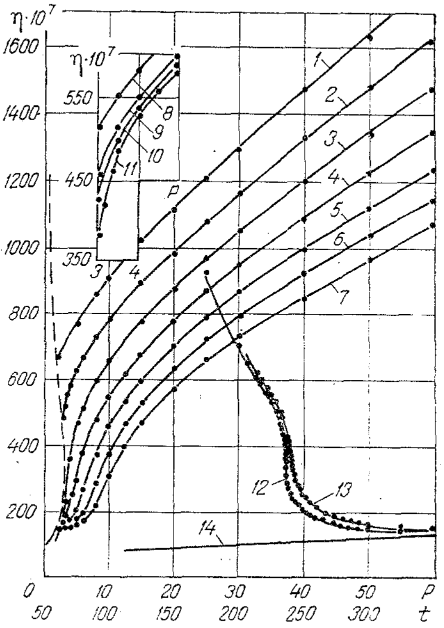

Fig. 2

Fig. 1. Viscosity of cyclohexane (experimental values) along isotherms, °C: 1) 8; 2) 10; 3) 13.5; 4) 15; 5) 17.5; 6) 20; 7) 25; 8) 35; 9) 50; 10) 75; 11) 100; 12) 125; 13) 150; 14) 175; 15) 200; 16) 250; 17) 300; 18) 350; 19) 400; 20) 275; 21) 281; 22) 281.5; 23) 285; 24) 325; 25) 375. $\eta \cdot 10^7$, Pa·sec; P, MPa; t, °C.

Fig. 2. Viscosity of n-hexane (experimental values): isotherms, °C: 1) 200; 2) 225; 3) 250; 4) 275; 5) 300; 6) 325; 7) 350; 8) 225; 9) 230; 10) 231; 11) 232; isobars, MPa: 12) 3.2; 13) 3.4; 14) 0.1.

computed equation for the viscosity, taking into account residual systematic errors in the quantities entering into the formula, their random errors, and errors in relating to temperature and pressure, showed that the relative error in the measurement of the viscosity for a confidence probability of $\alpha = 0.997$ in the vicinity of the liquid state does not exceed ±0.7% and does not exceed ±1.1% in the vapor and supercritical regions. Some increase in the error is possible near the critical region and near the phase transition curves, which results from the presence of small quantities of impurities in the substances being studied as well as errors in interpolating data on density, necessary for calculating the viscosity.

The viscosity of C_6H_{14} was measured in the temperature range 20-350°C and that of C_6H_{12} in the temperature range 6.7-400°C for pressures up to 60 MPa. The experiments were conducted with equal values of temperature and pressure along isotherms with steps of 25°C. The step in pressure was 5 MPa, and near phase transitions it was decreased to 0.1 MPa (Figs. 1 and 2).

Similar studies of the viscosity were carried out for cyclohexane near its melting curve. The measurements were carried out near the isotherms 6.7, 8, 10, 13.5, 15, 17.5, 25, and 35°C with gradual (every 0.05 MPa) increases in pressure up to the point at which the substance in the autoclave with the viscosimeter was transformed into the solid phase. Then, the pressure was lowered and the melting curve was approached from the solid state side, in order to exclude possible overcooling of the liquid. The system for creating and measuring the pressure was configured in such a way that it eliminated the possibility of crystallization of cyclohexane outside the autoclave with the measuring capillary. The experiments carried out showed that there was no sharp change in the viscosity on the isotherms when the melting pressure p_{melt} was attained. The characteristic behavior of viscosity isotherms without any anomalies is observed up to solidification of the substance (see Fig. 1), which, apparently, is related to the finite growth rate of the crystals during the formation of the solid phase. [The content of the principal component in the specimen being studied was 99.9% and that of impurities was 0.1%.]

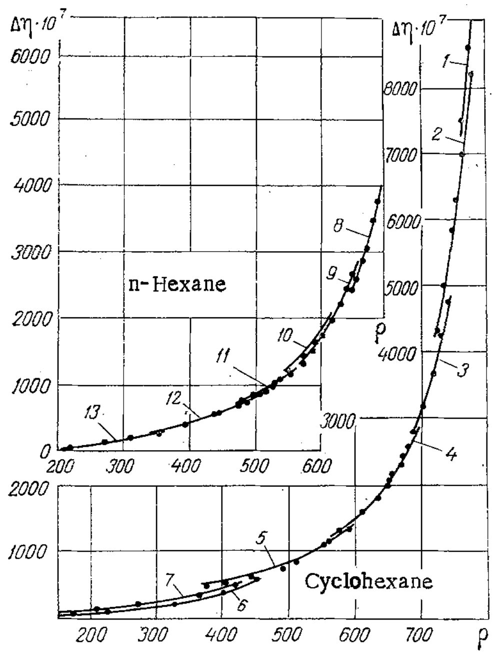

Fig. 3. Excess viscosity of n-hexane and cyclohexane as a function of density. The notation is the same as in Fig. 2.

The viscosity near critical region was measured for C_6H_{14} (t_{cr} = 234.7°C, p_{cr} = 3.058 MPa) along the isotherms 220, 225, 230, 232, and 233°C and along the isobars 3.2 and 3.4 MPa, and for C_6H_{12} (t_{cr} = 279.9°C, p_{cr} = 4.105 MPa) along the isotherms 275, 281, 281.5, and 285°C. Some 104 experimental points were obtained. In performing the measurements near the critical region, special attention was paid to the quality of temperature control (temperature fluctuations in the thermostat did not exceed 0.01°C), establishing an equilibrium state of the substance for given parameters, and taking into account corrections for determining temperature and pressure. Repeated tests were carried out for fixed values of t and p.

The experimental data on the viscosity of C_6H_{14} and C_6H_{12} were compared with the data in the literature. For n-hexane in the temperature range 20–275°C, our data agree with the results in [23] within 1.8%. For $t > 275°C$, no data are available in the literature for the viscosity of C_6H_{14}. For cyclohexane in the temperature range 20–90°C, the results of our work agree with the data in [24] within 1.5%. For higher temperatures, the data in [24] are systematically higher, and in addition, the deviations at 250°C constitute 25–30%. For $t > 250°C$, there is no information in the literature on changes in the viscosity of C_6H_{12}. It should be noted that in [24] values of the viscosity are presented for low temperatures and high pressures, for which, as our studies showed, cyclohexane is in the solid state.

On the basis of the experimental information obtained, we constructed different sections of the η-P-T surface for n-hexane and cyclohexane and we constructed detailed tables of η for uniform values of temperature and pressure. The graphical representation of the data in excessive viscosity–density coordinates (Fig. 3) revealed the presence of stratification along isotherms with increasing density.

We will now examine the status of the investigations of thermoconductivity of liquid hydrocarbons and petroleum products and the methods developed for calculating λ. It is well known that the theoretical methods for calculating the thermal conductivity of liquids cannot be used for petroleum products due to the absence of the necessary starting information (data on structure, nature of the intermolecular forces, individual hydrocarbon composition).

The existing semiempirical and empirical relations, as a check of these relations in [25] has shown, do not provide the necessary precision for calculating thermal conductivity. In this connection, it becomes necessary to create new methods for calculating the thermal conductivity of petroleum and petroleum products, which provide data with the precision required for practical purposes and which are based on easily accessible starting information.

A complex of computational formulas, which permit calculating the thermal conductivity in the temperature range 0-200°C and pressures 0.1-50 MPa, was developed from selected data on the properties of a large group of petroleum products of various origins and hydrocarbon composition [26-47].

Analysis of the existing methods for describing the temperature dependence of the thermal conductivity of liquids [48-50] showed that for petroleum products in the temperature range 0-200°C, the most useful equation is

$$\lambda_t = \lambda_{t_0}[1 - \alpha_\lambda (t - t_0)], \tag{16}$$

where λ_{t_0} is the coefficient of thermal conductivity for some fixed temperature (20 or 70°C), W/m•K; α_λ is the temperature coefficient of thermal conductivity, K^{-1}. The values of λ_{t_0} and α_λ are first computed from the following formulas:

$$\lambda_{t_0} = A_0 + A_1 M + A_2 (\rho_4^{t_0})^3 + A_3 \lg (n_D^{t_0}); \tag{17}$$

$t_0 = 20°C$ (petroleum products with $t_{cg} < 20°C$)

$$M \geqslant 400,\ A_0 = 0.2362;\ A_1 = 0.67\cdot 10^{-4};\ A_2 = -0.0292;\ A_3 = -0.674;$$

$$M < 400,\ n_D^{20} - \rho_4^{20} \geqslant 0.595;\ A_0 = -0.2269;\ A_1 = 0.168\cdot 10^{-3};$$

$$A_2 = -0.308;\ A_3 = 2.977;$$

$$M < 400,\ n_D^{20} - \rho_4^{20} < 0,595;\ A_0 = -0.1127;\ A_1 = 0.402\cdot 10^{-3};$$

$$A_2 = 0,475\cdot 10^{-3};\ A_3 = 0,729;$$

$t_0 = 70°C$ (petroleum products with $t_{cg} \geqslant 20°C$)

$$A_0 = 0,1023;\ A_1 = 0.948\cdot 10^{-4};\ A_2 = -0.120;\ A_3 = 0.389;$$

$$\alpha_\lambda = A_0 + A_1 (n_D^{t_0} - \rho_4^{t_0}) + A_2 / (n_D^{t_0} - \rho_4^{t_0}), \tag{18}$$

$$t_0 = 20°C\ A_0 = -0.02159;\ A_1 = 0.02517;\ A_2 = 0.00442;$$

$$t_0 = 70°C\ A_0 = 0.02215;\ A_1 = -0.01324;\ A_2 = -0.00802,$$

where M is the molar mass of petroleum product; $n_D^{t_0}$, index of refraction of the petroleum product for the D line of sodium at a temperature t_0; $\rho_4^{t_0}$, relative density of the petroleum product at a temperature t_0; t_{cg}, congealing temperature of the petroleum product.

A check of formula (16) showed that in using λ_{t_0} and α_λ obtained from formulas (17) and (18) the errors in the computation of thermal conductivity for petroleum products in the entire temperature range do not exceed 8% with an average of ∿2.5%.

In the absence of data on the index of refraction or the molar mass, their values can be computed from the formulas presented below. These formulas are based on the correlation between the physicochemical quantities of petroleum products and are obtained by the method of least squares from the experimental data:

$$n_D^{t_0} = A_0 + A_1 (\rho_4^{t_0})^2, \tag{19}$$

$$M = (n_D^{t_0} - \rho_4^{t_0}) \exp (B_0 + B_1 t_{\text{boil}}), \tag{20}$$

$$\frac{1}{M} = 0,0102 + 0,00825 (\rho_4^{20})^3 - 0,0604 \lg (n_D^{20}) - 0,00142 \lg (\nu_{20}\cdot 10^6) + 0.0034/(\nu_{20}\cdot 10^6), \tag{21}$$

where t_{boil} is the average boiling temperature of the petroleum product, °C; n_D^{20}, index of refraction at 20°C; ν_{20}, coefficient of kinematic viscosity at 20°C, m^2/sec; $t_0 = 20°C$: $A_0 = 1.218$; $A_1 = 0.358$; $B_0 = 4.5687$; $B_1 = 0.00453$; $t_0 = 70°C$: $A_0 = 1.232$; $A_1 = 0.332$; $B_0 = 4.7115$; $B_1 = 0.00396$.

Analysis of the existing methods for describing the pressure dependence of the thermal conductivity of liquids [29, 33, 50, 51] showed that for petroleum products in the temperature range 0-200°C and pressures 0.1-50 MPa, the most useful relation similar in form to the isothermal Tait equation in integral form for specific volumes is:

$$\lambda_{p,t} = \lambda_t / \left[1 - A_\lambda \ln \frac{B_\lambda(T) + P}{B_\lambda(T) + P_0}\right], \tag{22}$$

where A_λ is a coefficient equal for different petroleum products and does not depend on temperature and pressure ($A_\lambda = 0.1988$); $B_\lambda(T)$ is a function of temperature; P_0 is the atmospheric (or close to it) pressure, MPa; P is the pressure in MPa.

The values of λ_t are first computed from (16), while $B_\lambda(T)$ is computed from the following formula:

$$B_\lambda(T) = B_{\tau=0,31}(-3.1495 + 2.744\tau + 1.0203/\tau), \tag{23}$$

where $B_{\tau=0.31} = 38.42$ MPa; $\tau = \beta T$ is the reduced temperature; β is the temperature coefficient for the density, computed using Zenkevich's method [39], K^{-1}; T is the temperature, K.

A check established that the errors in computing the pressure dependence of the thermal conductivity for petroleum products over the entire pressure range do not exceed 3% with an average less than 1%.

The methods proposed for calculating the temperature and pressure dependences of the coefficient of thermal conductivity are recommended for petroleum products of straight-run distillation, products of thermal and catalytic cracking, petroleum fuel, and oil. As analysis shows, formulas (16)-(23) provide an accuracy for data on λ that is useful for engineering calculations. These formulas can easily be used in practice, since the starting quantities in them involve only physicochemical characteristics that are determined by standard methods.

LITERATURE CITED

1. P. V. Bridgman, Physics of High Pressures [Russian translation], ONTI—NKTP, Moscow (1935).
2. D. S. Kurumov, R. M. Murdaev, and B. A. Grigor'ev, "Experimental investigation of the P—v—T dependence of cyclohexane and benzoyl near the melting curve," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 3, 75-77 (1977).
3. B. A. Grigor'ev, A. S. Keramidi, V. K. Grachev, and Yu. L. Rastorguev, "Experimental investigation of the viscosity of sulphur hexafluoride," Teploenergetika, No. 9, 85-87 (1977).
4. C. B. Willingham, W. J. Taylor, J. M. Pignocco, and F. D. Rossini, "Vapor pressures and boiling points of some paraffin, alkylcyclopentane, alkylcyclohexane, and alkylbenzene hydrocarbons," J. Res. NBS, 35, 219-244 (1945).
5. B. A. Grigor'ev, R. M. Murdaev, and Yu. L. Rastorguev, "Experimental investigation of the P—v—T dependence of water," Teplofiz. Vys. Temp., 12, 83-91 (1974).
6. C. Drucker, E. Jimenon, and W. Kongro, "Vapor pressure of liquid substances at low temperatures," Z. Phys. Chem., 90, No. 5, 513-552 (1915).
7. Yu. L. Rastorguev, B. A. Grigor'ev, and R. M. Murdaev, "Refinement of the method of measuring the P—v—T dependence of liquids and gases by the spherical piezometer method," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 7, 69-70 (1973).
8. Yu. L. Rastorguev, B. A. Grigor'ev, and R. M. Murdaev, "Experimental investigation of the P—v—T dependence of cyclohexane in the liquid phase," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 1, 66-70 (1975).
9. B. A. Grigor'ev, R. M. Murdaev, and Yu. L. Rastorguev, "Experimental investigation of the P—v—T dependence of cyclohexane at high temperatures and pressures," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 3, 61-63 (1975).
10. R. M. Murdaev, "Experimental investigation of the saturation vapor pressure of cyclohexane," in: Problems in Petroleum and Gas [in Russian], Grozny (1977), pp. 58-59.
11. Yu. L. Rastorguev, B. A. Grigor'ev, and D. S. Kurumov, "Experimental investigation of P—v—T dependence of n-hexane in the liquid phase at high pressures," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 11, 61-64 (1976).
12. D. S. Kurumov, "Experimental investigation of specific volumes of n-hexane in the critical region," in: Problems in Petroleum Gas, Grozny (1977), pp. 54-55.
13. T. S. Akhundov, "Investigation of the thermophysical properties of aromatic hydrocarbons," Author's Abstract of Doctoral Dissertation, AzINKh, Baku (1974).
14. V. V. Altunin, Thermophysical Properties of Carbon Dioxide [in Russian], Standartov, Moscow (1975).
15. A. M. Sirota, "Investigation of caloric properties of water in a wide range of state parameters (25-1000 kgf/cm²; 0-700°C)," Author's Abstract of Doctoral Dissertation, VTI, Moscow (1970).
16. L. I. Safir, A. A. Gerasimov, and B. A. Grigor'ev, "Experimental investigation of isobaric heat capacity of cyclohexane," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 1, 61-65 (1975).

17. A. A. Gerasimov and B. A. Grigor'ev, "Experimental investigation of isobaric heat capacity of n-hexane," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 5, 46-48 (1978).
18. L. I. Safir and B. A. Grigor'ev, "Experimental investigation of isobaric heat capacity of n-hexane," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 2, 28-29 (1976).
19. D. R. Douslin and H. M. Huffman, "Low temperature thermal data on the five isomeric hexanes," J. Am. Chem. Soc., 68, 1704-1708 (1946).
20. M. P. Vukalovich and I. I. Novikov, Engineering Thermodynamics [in Russian], Energiya, Moscow (1968).
21. M. T. Kaganer, "Maxima of thermodynamic properties and transitions from gas to liquid in the supercritical region," Zh. Fiz. Khim., 32, 332-340 (1958).
22. I. F. Golubev and N. A. Agaev, Viscosity of Limiting Hydrocarbons [in Russian], Azerneshr, Baku (1964).
23. I. F. Golubev and N. E. Gnezdilov, Viscosity of Gaseous Mixtures [in Russian], Standartov, Moscow (1971).
24. S. O. Guseinov, "Investigation of the viscosities of olefins, naphthenes, paraffin hydrocarbons and benzene at different temperatures and pressures," Author's Abstract of Candidate's Dissertation, AzINKh, Baku (1973).
25. A. I. Svidchenko, B. A. Grigor'ev, and G. F. Bogatov, "Evaluation of methods for calculating thermal conductivity of liquid petroleum products," Abstracts of Reports at the All-Union Conference on the Theory and Practice of Rectification of Petroleum Mixtures [in Russian], BashNIINP, Ufa (1975), pp. 138-141.
26. B. A. Grigor'ev, "Investigation of the thermophysical properties of petroleum and short distillates of Ozeksuat petroleum," Author's Abstract of Candidate's Dissertation, OTIPP, Odessa (1967).
27. V. Z. Geller, "Investigation of thermophysical properties of Mangyshlaksk petroleum and its distillates," Author's Abstract of Candidate's Dissertation, Energy Institute, Moscow (1968).
28. Yu. L. Rastorguev, "Investigation of the thermal conductivity of water, individual hydrocarbons, petroleum, petroleum products, organosilicon compounds and liquid solutions over a wide range of state parameters," Authors' Abstract of Doctoral Dissertation, AzINKh, Baku (1971).
29. Yu. L. Rastorguev, B. A. Grigor'ev, and G. F. Bogatov, "Thermal conductivity of petroleum and petroleum products," in: Heat and Mass Transfer, Vol. VII [in Russian], Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk.
30. B. A. Grigor'ev, G. F. Bogatov, and Yu. L. Rastorguev, "Experimental investigation of the density and thermal conductivity of thermal cracking kerosene and its short distillates," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 7, 63-67 (1973).
31. G. F. Bogatov, B. A. Grigor'ev, and Yu. L. Rastorguev, "Experimental investigation of the thermal conductivity of the products of catalytic cracking and their distillates," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 7, 86, 112 (1974).
32. G. F. Bogatov, B. A. Grigor'ev, and R. A. Andolenko, "Investigation of the thermophysical properties of M-20 G oil," Izv. Vyssh. Uchebn. Zaved., Neft' Faz, No. 6, 62, 90 (1974).
33. Yu. L. Rastorguev, B. A. Grigor'ev, G. F. Bogatov, et al., "experimental investigation of the viscosity and thermal conductivity of Samotlorskii petroleum and its distillates," in: Thermophysical Properties of Gases [in Russian], Nauka, Moscow (1976), pp. 75-81.
34. Yu. L. Rastorguev, B. A. Grigor'ev, G. F. Bogatov, et al., "Experimental investigation of the thermal conductivity of the distillates of petroleum mixtures from the Zhetybai and Uzen' deposits," Abstracts of Reports at the All-Union Conference on the Theory and Practice of Rectification of Petroleum Mixtures [in Russian], BashNIINP, Ufa (1975), pp. 100-103.
35. A. I. Svidchenko, "Investigation of the thermal conductivity of petroleum, petroleum distillates, and commercial petroleum products," Author's Abstract of Candidate's Dissertation, Grozny, GNI (1977).
36. N. V. Tsederberg and V. N. Popov, "Investigation of the thermal conductivity of T-1 kerosene and its heavy distillates," Teploenergetika, No. 8, 61-64 (1957).
37. V. N. Popov and N. V. Tsederberg, "Thermal conductivity of liquid fuels," Teploenergetika, No. 11, 72-76 (1958).
38. V. N. Popov, N. V. Tsederberg, and N. A. Morozova, "Experimental investigation of the thermal conductivity of mixtures of petroleum products," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 6, 55-57 (1964).

39. V. B. Zenkevich, "Experimental investigation of the thermophysical properties of liquid fuels and oils," Author's Abstract of Candidate's Dissertation, Energy Institute, Moscow (1961).
40. G. D. Tatevosov, "Experimental investigation of the thermal conductivity of toluol and cooling oils," Author's Abstract of Candidate's Dissertation, OTIKhP, Odessa (1971).
41. F. A. Kuliev, "Investigation of the influence of the hydrocarbon composition, method, and degree of refinement of transformer oils on their thermophysical properties," Author's Abstract of Candidate's Dissertation, AzINKh, Baku (1971).
42. R. Zokirov, "Investigation of viscothermal properties and thermal conductivity of short oil distillates and finished oils prepared by different methods and with different degrees of refinement obtained from the new petroleum from the Azerbaidzhan Sangachal More," Author's Abstract of Candidate's Dissertation, AzINKh, Baku (1972).
43. Kh. Zibland and M. T. Dapri, "Thermal conductivity of D. Eng. M. D. 2495 kerosene in the temperature range from 15 to 325°C at pressures up to 200 atm," Raket. Tekh., 31, 118-121 (1961).
44. K. A. Zeinalov, "Investigation of the thermal conductivity of finished oils obtained from petroleum from O. Peschanyi," Azerb. Neftyanoe Khozyaistvo, No. 2, 32-34 (1969).
45. A. V. Kozyukov, "Thermal conductivity of B-70 benzene, T-1 kerosene, and T-5 fuel in the liquid phase," in: Thermophysical Properties of Some Aviation Fuels in the Liquid and Gaseous States [in Russian], Oborongiz, Moscow (1962), pp. 94-108.
46. G. Kh. Mukhamedzyanov, "Thermal conductivity of liquid petroleum products," Tr. KKITI, im. S. M. Kirova, No. 39, Ser. Teplo- i Massoobmen, KKhTI, , Kazan (1968), pp. 49-53.
47. D. T. Jamieson and J. S. Tudhope, "A simple device for measuring the thermal conductivity of liquids with moderate accuracy," J. Inst. Petr., 50, 150-153 (1964).
48. N. V. Tsederberg, Thermal Conductivity of Gases and Liquids [in Russian], State Energy Institute, Moscow (1963).
49. L. P. Fillipov, Investigation of the Thermal Conductivity of Liquids [in Russian], Moscow State University, Moscow (1970).
50. A. Misnar, Thermal Conductivity of Solids, Liquids, Gases, and Their Compositions [Russian translation], Mir, Moscow (1968).
51. J. M. Lenoir, "Effect of pressure on thermal conductivity of liquids," Petr. Refiner, 36, 162-164 (1957).

SHIROKOV'S FORMULA CONNECTING THE TRANSFER PROPERTIES OF LIQUIDS WITH THE VELOCITY OF SOUND

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According to existing data for u, η, λ, it is established that Shirokov's formula can become a quantitative relation if we introduce into it a dimensionless quantity ε, which depends on the temperature and pressure.

Starting from the idea of heat transfer by means of hyperacoustic oscillations of the medium, and assuming the mean free paths of the molecules in these processes to be equal, Shirokov [1] established a relation between the translational properties and the velocity of sound in liquids:

$$\frac{\eta}{\lambda}=\frac{T}{u^2}. \tag{1}$$

Our investigations have shown that the Shirokov complex $u^2\eta/T\lambda$* at any temperature and pressure for different liquids always differs from unity. Denoting the deviations of this complex by ε, Eq. (1) can be represented in the form

$$\frac{u^2\eta}{T\lambda}=\varepsilon. \tag{2}$$

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*The Shirokov complex in [2] is represented as $\lambda/\eta=u^{m(T)}/A(T)$.

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