4. E. I. Marchenkov, Author's Abstract of Candidate's Dissertation, Institute of Heat and Mass Transfer, Minsk (1975).
5. G. Springer and F. Faubert, J. Chem. Phys., 58, 4080 (1973).
6. P. C. Jain and S. C. Saxena, Chem. Phys. Lett., 36, No. 4 (1975).
7. J. B. Ubbink and W. J. de Haas, Physica, 10, No. 7 (1943).
8. I. F. Golubev and I. B. Shpagina, Gaz. Prom-st', No. 7 (1966).
9. H. L. Johnston and E. R. Grilly, J. Chem. Phys., 14, No. 4 (1946).
10. A. Eucken, Z. Phys., 13, No. 12, 1101 (1911); 14, No. 8, 324 (1913).
11. W. G. Kannuluik and E. H. Carman, Proc. Roy. Soc., B65, 701 (1952).
12. N. B. Vagraftik and N. Kh. Zimina, At. Énerg., No. 19 (1965).
13. L. S. Zaitseva, Zh. Tekh. Fiz., 29, 4 (1959).
14. P. Joannin and Wilson, in: Second ASME Symposium on Thermophysical Properties, Academic Press, New York (1962), p. 418.
15. P. Tufeu, "Étude experimentale en fonction de la temperature et de la pression de la conductivité thermique de l'ensemble des gas rares et des mélanges helium-argon," L. Université de Paris, VI (1971).
16. J. F. Kerrisk, "The thermal conductivity of helium," Dissertation, University of New Mexico (1968).

APPARATUS FOR COMPLEX THERMOPHYSICAL STUDIES OF LIQUIDS AT HIGH STATE PARAMETERS IN THE MONOTONIC HEATING REGIME

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UDC 536.2.083

Experimental apparatus used and results obtained in a complex of studies of thermophysical properties of n-undecane and n-tridecane are described.

The thermal conductivity λ and heat capacity c_p of liquids have been studied significantly less than other physical properties, and for the majority of materials the experimentally studied range of change of thermophysical properties with temperature is not large. Data on the effect of pressure on λ and c_p are very sparse. The difficulties in such studies are related mainly to realization of existing methods and experimental devices which will function in the range of high temperatures and pressures.

For studies of λ in liquids, in recent times nonstationary methods have become ever more popular, in particular, regular type I regime methods [1]. The theory of the regular type I regime was developed in the linear variant, so that these methods are convenient only at fixed temperatures. At high temperatures these methods require almost as much experimental time as stationary ones and, moreover, do not allow determination of the temperature dependence of λ from one experiment. Thus, monotonic heating methods deserve special attention, since they allow determination of the temperature dependences of thermophysical properties over a wide temperature range from one experiment which requires a relatively small amount of time.

The first attempt in this direction was that of Kraev [2], who proposed one of the simplest variants of the λ-calorimeter for measurement of λ in liquids close to room temperature. The method can be used successfully at moderate pressures and temperatures. Unfortunately, his calorimeter is not capable of high-accuracy measurements for operation at high pressures. In order to solve this problem, it is necessary to provide a more refined theoretical basis for the method and develop an improved calorimetric device. Somewhat later a similar closed-layer method was proposed by Platunov for studies of dispersed materials [3].

Azerbaidzhan Polytechnic Institute, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 32, No. 5, pp. 825-834, May, 1977. Original article submitted May 18, 1976.

The Kraev–Platunov system in the linear variant was used by Cherneeva for studies of λ in water and water vapor at high state parameters [4]. She used the infinite cylinder variant with adiabatized end faces. The working formula was obtained from the thermal balance equation without consideration of the temperature dependence of thermophysical properties and the nonlinearity of heating and without analysis of the temperature field of the calorimetric system.

The necessity of studying thermophysical properties of a wide range of organic liquids in the supercritical state region compelled the authors to consider the nonlinear theory of the process, considering the temperature dependence of the thermophysical properties. As a result, monotonic heating methods were developed for study of λ and c_p of liquids over a wide range of temperature and pressure.

I. The calorimetric device for studies of λ consists of a hollow metallic block and solid copper rod mounted coaxially. The annular gap between them is of constant thickness and is filled with the liquid to be studied. An electric heater is uniformly distributed over the block surface and produces a continuous monotonic increase in calorimeter temperature. The bar is then heated by heat supplied to it through the closed layer of the material studied. Under monotonic heating conditions the temperature field of the cylindrical layer obeys the nonlinear thermal-conductivity equation, whose solution produces the following formula [5]:

$$\lambda(\bar{t}) = \frac{h}{\bar{F}}\,\frac{c_c b_c}{\vartheta - \vartheta^0}\left(1 + \Delta\sigma_c + \Delta\sigma_f + \Delta\sigma_\vartheta\right) - \Delta\lambda.$$

II. The calorimetric device for determination of c_p consists of a hollow metal block with a concentrically installed metal ampule, filled with the liquid to be studied. The entire system is heated monotonically by a heater distributed over the outer surface of the block. The ampule with the liquid to be studied is heated by heat passing through the thin air gap, whose thermal conductivity is considered known.

The formula used in calculation follows from the thermal balance equation for the calorimetric system and has the form [6]

$$c_p(t) = \frac{1}{\gamma V_0}\left[\frac{k(t)\,\vartheta(\tau)}{b(\tau)} - c_a(t)\right].$$

The quantities k(t) and $c_a(t)$ appearing in the formula are determined by special calibration experiments [7]. However, at high pressures the coefficient k may be a function not only of temperature, but also of pressure, due to the change in the air gap. Calculation of the change in the gap under the influence of pressure and the calibration experiments performed showed that this correction is practically equal to zero at pressures up to 500 kg/cm².

On the basis of these theoretical considerations the authors have constructed an apparatus (cλ-calorimeter) for complex thermophysical measurements [8].

III. The dynamic cλ-calorimeter is designed for studies of λ and c_p of liquids in the temperature range from 30 to 400°C at pressures up to 500 bar. The duration of an experiment in the indicated temperature range does not exceed 1 h at a temperature differential of 3-10°. Relative errors in determination of λ and c_p do not exceed 2 and 2.5%, respectively. Reproducibility of experimental data for one and the same state parameters lies in the limits 1-1.3%. Measurements were performed under monotonic heating conditions. The cλ-calorimeter consists of calorimetric devices for measurement of λ and c_p, pressure control and filling systems, electrical measurement circuitry, and a heater system.

1. A diagram of the cλ-calorimeter is presented in Fig. 1. On the mounting plate are installed calorimeters I (λ-calorimeter) and II (c-calorimeter) and distribution valves 12. Within the control panel is installed equipment for system evacuation, filling, and pressure generation. The forevacuum pump and electrical measurement circuitry, consisting of a potentiometer and galvanometer, are located outside the main body of the device. Each of the calorimeters consists of a massive metallic block 6, surrounded by a thermal insulation envelope 10. The envelope around the block forms a closed air space which is heated together with the block, as a result of which reliable and effective thermal shielding of the block surface is achieved during the entire experiment. The dimensions of the air cavity and the

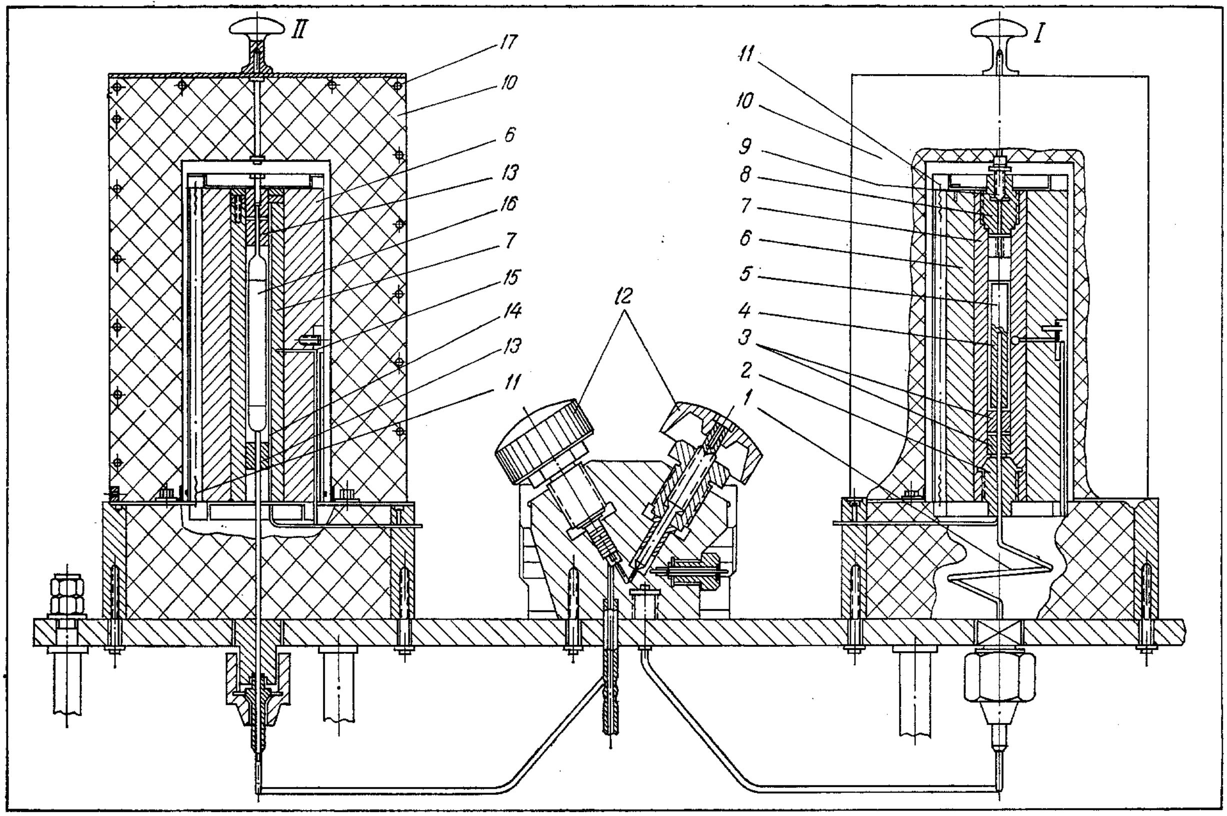

Fig. 1. Diagram of cλ-calorimeter.

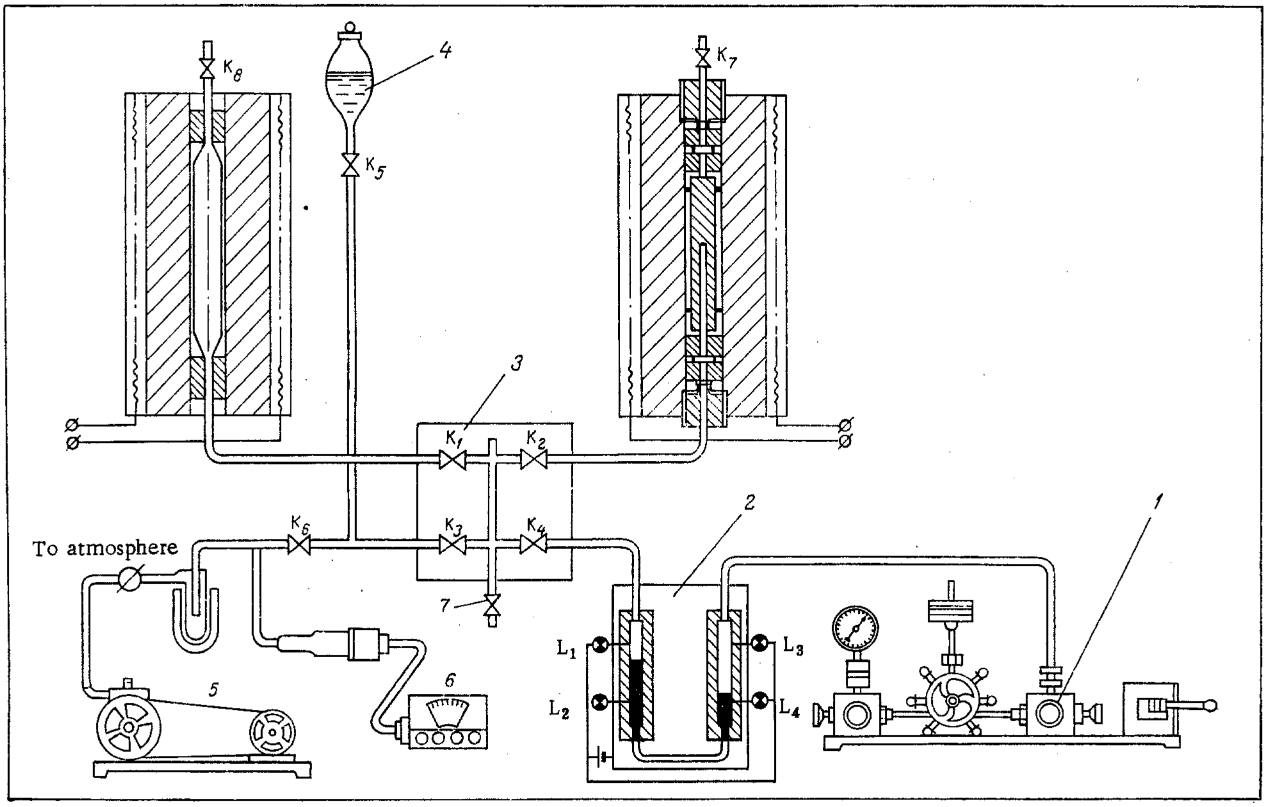

Fig. 2. Calorimeter pressure and filling system.

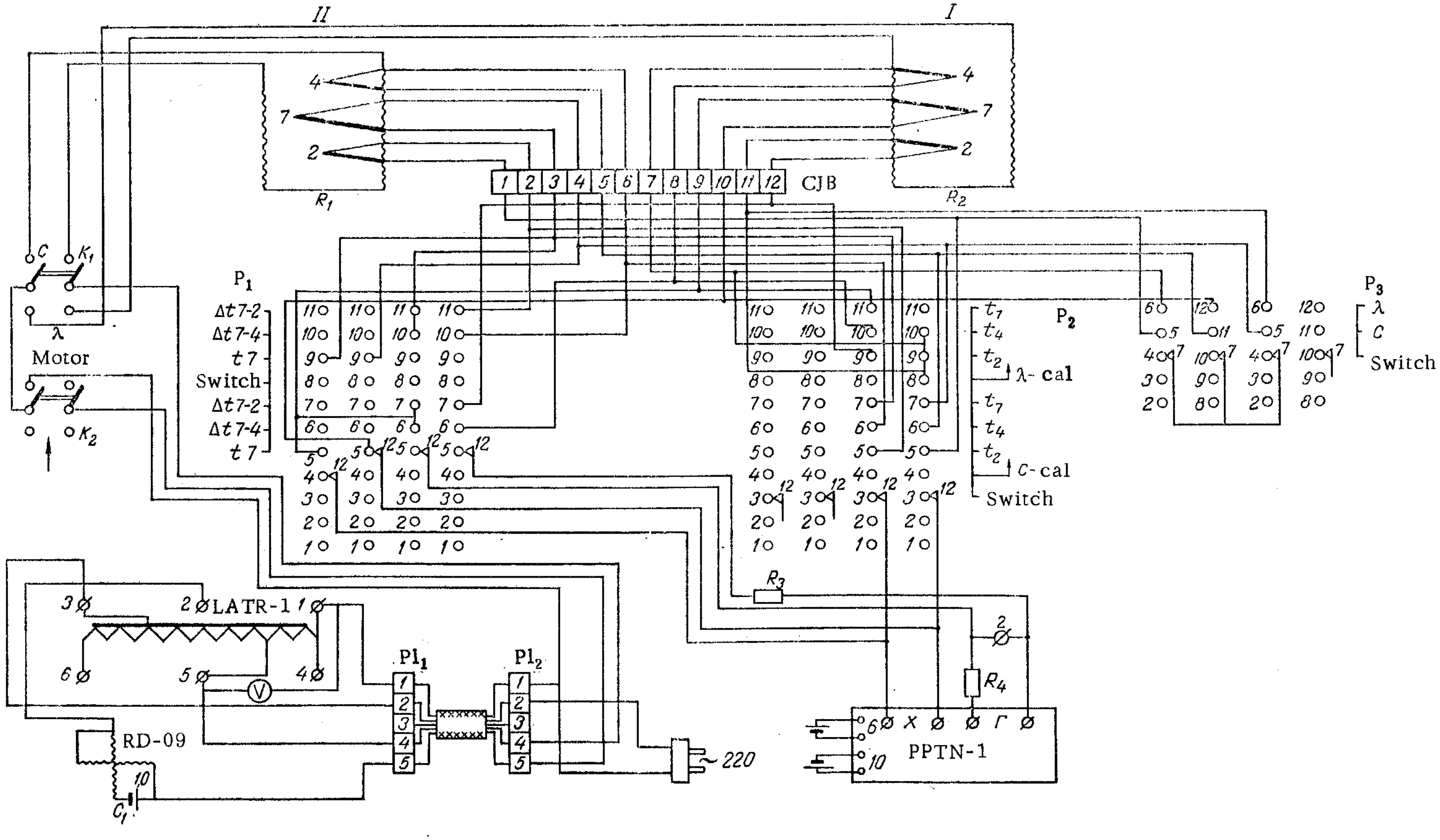

Fig. 3. Temperature measurement and electrical supply circuits.

TABLE 1. Thermal conductivity λ [W/(m·deg)] and Heat Capacity c_p [kJ/(kg·deg)] of n-Undecane vs Temperature and Pressure

t, °C	$\lambda\cdot10^4$	$c_p\cdot10^2$	$\lambda\cdot10^4$	$c_p\cdot10^2$	$\lambda\cdot10^4$	$c_p\cdot10^2$	$\lambda\cdot10^4$	$c_p\cdot10^2$	$\lambda\cdot10^4$	$\lambda\cdot10^4$	$c_p\cdot10^2$
	P = 1 kg/cm²		100		200		300		400	500	
34,6	1295	214	1335	212	1372	209	1409	207	1442	1475	204
48,4	1257	218	1308	215	1345	213	1382	211	1423	1447	207
61,5	1238	222	1282	219	1315	217	1353	214	1390	1432	210
74,2	1204	226	1245	223	1282	220	1325	217	1360	1395	214
88,4	1175	230	1224	227	1255	224	1302	222	1338	1367	217
99,0	1145	233	1193	229	1240	227	1278	224	1310	1350	220
110,5	1117	236	1177	232	1217	230	1250	227	1290	1330	223
122,3	1090	239	1148	236	1184	233	1235	230	1272	1308	226
134,4	1063		1116		1158		1207		1247	1283	
144,7	1038	245	1095	242	1145	239	1190	236	1228	1270	231
154,5	1023	247	1090	245	1132	242	1170	239	1220	1262	234
165,5	1008	250	1055	247	1107	245	1158	242	1203	1243	236
175,5	992	253	1042	250	1096	247	1147	244	1200	1232	239
185,5	972	256	1019	253	1072	250	1142	247	1180	1220	241
195,5			1008	256	1068	252	1122	249	1168	1208	247
205,4			990	259	1052	255	1108	252	1150	1198	247
216,2			985	263	1047	258	1102	255	1154	1195	249
228,3			960	267	1025	262	1087	258	1140	1182	253
236,6			950	269	1008	264	1078	261	1132	1187	254
246,8			942	272	1012	267	1070	263	1135	1172	257
254,5			932	275	1002	270	1065	265	1118	1168	259
265,4			922	279	998	273	1054	269	1115	1156	262
274,2			924	282	988	276	1055	272	1108	1158	264
284,3			910	286	980	279	1045	275	1100	1150	267
295,5			902	290	970	283	1050	278	1098	1148	270
302,6			895	292	972	285	1040	280	1090	1147	271
310,5			888		972		1032		1092	1155	
336,4			880		956		1018		1078	1140	
354,2			874		942		1007		1075	1122	
372,6			868		944		1005		1070	1125	
380,5			865		947		1002		1072	1122	
396,2			858		938		998		1058	1118	
404,5			855		935		997		1058	1115	

emissivities of block and shell surfaces are selected so that heat transfer through the air interlayer is accomplished mainly by thermal conductivity. Because of the envelope, the heat liberated by heater 11 is dissipated mainly in heating the block. The stability of heating increases from experiment to experiment. The envelope shell is cooled by water through coil 17, soldered to the inner surface. The metal block is of complex construction. A tube 7 made of 1Kh18N9T stainless steel is pressed into a massive copper cylinder. The end faces of the λ-calorimeter are hermetically sealed by rubber seals 2 and 8. Within the cavity of the tube is located a copper rod 5, whose end faces are separated from the rubber seals by guard cylinders 3. The gap between these components is filled with the liquid to be studied. The size of this gap, identical over the entire rod surface, is ensured by calibrated quartz spheres pressed into the rod and protected by small cylinders. The latter are intended to equalize the temperature field around the rod and thus they have good thermal contact with the tube walls and much poorer thermal contact between each other and the rubber seals. Attached to the lower seal 2 are tube 1 for filling the calorimeter with liquid and guide 4 for the rod thermocouple. The outer end of tube 1 has a rubber tail piece for connection to the filling and pressure-generation systems. Seal 8 has an orifice for filling and washing the calorimeter, also provided with a rubber seal 9.

Nonuniformity of the temperature field over the height of the block can be monitored by five thermocouples. For this purpose five radial orifices, 1.5 mm in diameter, which approach within 1 mm of the working surface, are drilled in the block.

The c-calorimeter differs in that within tube 7 there is installed an ampule 16 made of EI-247 stainless steel. The ampule end faces are connected to tubes for filling with liquid. Two guard cylinders 13 flush with the internal tube wall center the ampule within the tube and form an isothermal cavity about the ampule. The air interlayer between ampule and tube forms the working layer of the calorimeter. The heat-transfer coefficient of the calorimeter is a "constant" of the particular device and is found from calibration experiments.

TABLE 2. Thermal Conductivity λ [W/(m·deg)] and Heat Capacity c_p [kJ/(kg·deg)] of n-Tridecane vs Temperature and Pressure

t, °C	$\lambda \cdot 10^4$	$c_p \cdot 10^2$	$\lambda \cdot 10^4$	$c_p \cdot 10^2$	$\lambda \cdot 10^4$	$c_p \cdot 10^2$	$\lambda \cdot 10^4$	$c_p \cdot 10^2$	$\lambda \cdot 10^4$	$\lambda \cdot 10^4$	$c_p \cdot 10^2$
	P = 1 kg/cm²		100		200		300		400	500	
34,6	1336	210	1376	208	1412	205	1446	203	1480	1515	201
48,4	1312	213	1357	211	1387	208	1422	206	1450	1485	203
61,5	1290	217	1318	214	1370	211	1395	209	1425	1457	206
74,2	1252	220	1285	217	1335	214	1370	212	1407	1432	208
88,4	1235	224	1270	221	1300	218	1348	215	1378	1407	213
99,0	1205	226	1240	223	1285	220	1320	218	1358	1390	214
110,5	1180	229	1235	226	1270	222	1305	220	1338	1372	216
122,3	1157	232	1207	229	1255	226	1295	223	1322	1360	219
134,4	1138	235	1182	231	1222	228	1266	225	1305	1332	221
144,7	1115	237	1155	234	1200	230	1250	228	1290	1324	223
154,5	1098	239	1135	236	1195	233	1240	230	1270	1305	226
165,5	1082	242	1127	239	1180	235	1220	232	1264	1300	228
175,5	1060	245	1120	241	1160	238	1212	235	1250	1285	230
185,5	1040	248	1095	244	1155	240	1198	237	1240	1275	233
195,5	1022	251	1082	246	1135	242	1190	239	1228	1265	235
205,4	1015	254	1070	250	1125	245	1175	242	1215	1250	237
216,2	1004		1058	253	1118	248	1167	244	1210	1247	239
228,3			1042	256	1107	251	1150	247	1197	1228	242
236,6			1027	258	1090	254	1142	250	1190	1222	244
246,8			1012	262	1075	257	1138	252	1180	1218	247
254,5			1008	265	1072	259	1125	254	1168	1208	249
265,4			990	269	1062	262	1117	257	1165	1205	251
274,2			988	272	1055	265	1110	260	1160	1200	252
284,3			975	275	1045	268	1102	262	1148	1192	255
295,5			968	279	1042	272	1095	266	1146	1190	258
302,6			960	281	1035	274	1085	268	1140	1185	260
310,5			957		1025		1082		1140	1190	
319,7			952		1022		1077		1132	1180	
328,5			955		1017		1075		1130	1185	
336,4			942		1012		1070		1125	1178	
344,5			945		1010		1067		1124	1180	
354,2			940		1004		1062		1118	1170	
372.6			933		1005		1062		1116	1172	
380,5			928		1002		1060		1115	1170	
388,4			930		1003		1057		1112	1168	
396,2			925		998		1055		1112	1165	
404,5			928		996		1054		1110	1160	

The thermocouple that measures ampule temperature is mounted in a thin steel needle 14, attached to the ampule wall, while the other thermocouples are installed within needle 15. Opposite needle 14 on the inner surface of the tube there is a longitudinal groove 3 × 3 mm.

2. The pressure and filling system is designed to generate and measure pressure in the vessel, evacuate the vessel, and fill the calorimeters with the liquid to be studied (Fig. 2).

The system consists of press 1, mercury divider 2, distribution valve system 3, filling funnel 4, and forevacuum pump 5 with vacuum gauge 6. The distribution valve system allows the calorimeter to be filled with liquid and transmits pressure to the working volume of the calorimeter. The system body has a channel common to all four valves, joining them into one system. Openings below the body connect the system with the press, the vacuum system, and the λ- and c-calorimeters. Each of the valves can close an opening into the body, thus dividing one volume from the other.

Four signal lamps, L_1-L_4, are used to control the mercury level in the divider, with power fed to them through the mercury column. The system is filled with liquid as follows. For operation of the λ-calorimeter valves K_1 and K_5 are closed, and valves K_2, K_3, K_4, and K_6 are open. A vacuum is created in the system with forevacuum pump 5. The vacuum is monitored by vacuum gauge 6. Then valve K_6 is closed and K_5 is opened, as a result of which the entire system is filled with the liquid to be studied. The c-calorimeter is filled in a similar manner. To drain the system all valves are opened and all the liquid flows out through tube 7.

3. The temperature measurement and electrical supply circuits are shown in Fig. 3. All temperature measuring thermocouples are connected to the CJB (cold junction block) which stabilizes the temperature of the thermocouple cold junctions. The supply circuitry consists of a high power LATR-1 autotransformer, two electric heaters R_1 and R_2, a voltage regulator,

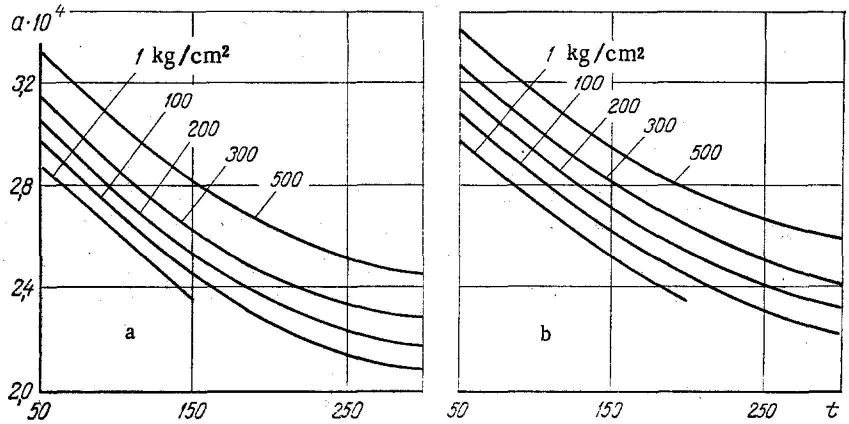

Fig. 4. Thermal diffusivity of n-undecane (a) and n-tridecane (b) at high temperatures and pressures. t, °C; $a\cdot10^4$, $m^2\cdot g$.

and several switches on the front control panel of the unit. Switch K_1 transfers power from one heater to the other, i.e., selects the λ-calorimeter or the c-calorimeter. The calorimeters are heated by the heaters which are fed by the autotransformer. During the course of the experiment the voltage from the autotransformer increases linearly as the output contact is shifted by the RD-09 motor through a reduction drive. The drive is provided with a mechanism for continuously adjusting the rotation speed of the LATR control. The calorimeter heating rate depends on the value of the initial voltage and its rate of increase. The initial voltage is established manually and is monitored by a voltmeter. Switch K_1 connects one of the calorimeters. When K_2 is switched on, voltage is applied simultaneously to a heater and to the RD-09 motor. The temperature measurement circuitry uses a potentiometer scheme, multiple channel thermocouple switches P_1, P_2, P_3, and a mirror galvanometer. Switch P_3 connects the measurement system to the thermocouples of either the λ- or c-calorimeters. Switches P_1 and P_2 connect one or the other calorimeter thermocouple to the system: P_1 provides temperature differential information and P_2, the time delay.

4. The rod (ampule) temperature and temperature differential across the layer ϑ were measured experimentally by an R-306 potentiometer, class 0.015, mirror galvanometer M17/4, and 51 SD stopwatch with 0.1-sec divisions. Temperature measurements were made with Nichrome–Constantan thermocouples calibrated at the Mendeleev All-Union Scientific-Research Institute of Metrology. The rod (ampoule) temperature was measured at discrete emf values on the potentiometer. Times of thermo-emf compensation with established emf values across the potentiometer were recorded by the stopwatch. Such a temperature–time recording of the curve $t_c(\tau)$ makes it possible to calculate $b(\tau)$ without recourse to graphical differentiation of the curve $t(\tau)$. Measurements were performed at $b = 0.1$ deg/sec ($U_{init} = 120$ V) with the rate of change of regulator voltage $k = 1.3\cdot10^{-2}$ V/sec. Pressure was generated and measured by an MP-600 piston manometer, class 0.05, and reference manometers. The apparatus described allowed measurements of λ and c_p in a wide class of substances (aromatic, paraffin, and olefin hydrocarbons) in the supercritical state region [9-14]. Tables 1 and 2 present experimental values of λ and c_p for paraffin hydrocarbons (n-undecane and n-tridecane). All corrections used in the method of [15] were introduced into the calculations. Methods of estimating the corrections $\Delta\sigma_c$, $\Delta\sigma_f$, and $\Delta\sigma_\vartheta$ for various state regions are presented in [5, 10, 13]. Calculation reveals that the magnitudes of these corrections under our experimental conditions comprise $5.5\cdot10^{-2}$, $7.5\cdot10^{-4}$, and $6.8\cdot10^{-4}$. Measurements were performed every 10-12°. On the basis of the data obtained, Fig. 4 presents isobars and isotherms for n-tridecane. Curves for n-undecane have a similar form.

With the results obtained herein and use of data on γ [16], for the first time the character of the behavior of the thermal diffusivity of hydrocarbons at high temperatures and pressures has been established (Fig. 4). It has been established that the character of the change in thermal conductivity of these hydrocarbons at high temperatures and pressures is also intrinsic to thermal diffusivity.

NOTATION

$\bar{t} = t_c + {}^1/_2\vartheta$; c_c, heat capacity of copper rod; h, $\bar{F}$, thickness and mean cross section of liquid layer; b, heating rate; ϑ^0, correction to indication of thermocouples measuring temperature differential across layer; $\Delta\sigma_c$, $\Delta\sigma_f$, and $\Delta\sigma_\vartheta$, corrections for heat capacity, curvature, and nonlinearity; $\Delta\lambda$, correction for heat transfer from block to rod through "parasitic" channels; k(t), thermal conductivity of air gap; c_a, heat capacity of ampule; γ, density of liquid.

LITERATURE CITED

1. Ya. M. Naziev, Author's Abstract of Doctoral Dissertation, GNIÉI, Moscow (1970).
2. O. A. Kraev, Zavod. Lab., No. 2 (1960).
3. E. S. Platunov, Izv. Vyssh. Uchebn. Zaved., Priborostr., No. 1, 4 (1961).
4. L. I. Cherneeva, in: Thermophysical Properties of Gases [in Russian], Nauka, Moscow (1970).
5. R. A. Mustafaev and E. S. Platunov, Teplofiz. Vys. Temp., 10, No. 6 (1972).
6. R. A. Mustafaev and V. V. Kurepin, Teplofiz. Vys. Temp., 11, No. 1 (1973).
7. R. A. Mustafaev, Izv. Vyssh. Uchebn. Zaved., Priborostr., No. 7 (1971).
8. R. A. Mustafaev, Author's Abstract of Doctoral Dissertation, Baku (1973).
9. R. A. Mustafaev, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz., No. 5, 7 (1972).
10. R. A. Mustafaev, Izv. Vyssh. Uchebn. Zaved., Énerg., No. 7, 9 (1972).
11. R. A. Mustafaev, Zh. Fiz. Khim., No. 4, 10 (1973).
12. R. A. Mustafaev, Inzh.-Fiz. Zh., 24, No. 4 (1973).
13. R. A. Mustafaev, Teplofiz. Vys. Temp., 10, No. 4 (1972); 12, No. 4 (1974).
14. R. A. Mustafaev, D. M. Gabulov, and A. A. Abbasov, Izv. Vyssh. Uchebn. Zaved., Énerg., No. 7 (1975); Izv. Vyssh. Uchebn. Zaved., Neft' Gaz., No. 8 (1975).
15. E. S. Platunov, Thermophysical Measurements in the Monotonic Regime [in Russian], Énergiya, Moscow (1973).
16. A. K. Doolittle, Chem. Eng. Data, 9, 2 (1964).

INVESTIGATION OF THE EFFECT OF A MAGNETIC FIELD ON THE THERMOPHYSICAL CHARACTERISTICS OF FERROMAGNETIC SUSPENSIONS

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UDC 536.22:532.135

The effect of a constant magnetic field on the heat-transfer process in ferromagnetic suspensions has been experimentally investigated. The effective thermal conductivity of ferromagnetic suspensions is shown to be anisotropic in character.

Attempts to intensify technological processes and control transfer processes in fluid systems have recently led to the development of fluids sensitive to magnetic fields. These include ferrosuspensions whose rheological properties are a certain function of the external magnetic field. However, although we already know a good deal about the magnetorheological characteristics of ferrosuspensions [1-2], information about the effect of a magnetic field on their thermophysical characteristics is still very scarce [3].

We have investigated the effect on the thermophysical characteristics (thermal conductivity, thermal diffusivity, specific heat) of ferrosuspensions by varying the type and concentration of the disperse phase, the strength of the magnetic field, and the orientation of the field relative to the direction of the temperature gradient.

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