where $(\partial\lambda/\partial t)^{av}_{P_{atm}}$ is the mean value of the derivative at atmospheric pressure (see Table 1) and A is a coefficient taking account of the change in the temperature dependence of the thermal conductivity of the polymethylphenyl-siloxanes on the pressure. As computations for the polymers investigated showed,

$$A = (0.4 \cdot 10^5 p^2 - 0.144 \cdot 10^{-2} p) 10^{-3}. \qquad (4)$$

The deviations of the experimental results from those calculated by means of (1) do not exceed ± 3%.

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MEASURING THE VISCOSITY OF SUPERHEATED LIQUIDS
AT HIGH PRESSURES

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UDC 532.782+532.13

An experimental apparatus for measuring the viscosity of superheated liquids at high pressures is described, together with the corresponding measuring technique; results of viscosity measurements are presented for superheated n-hexane.

The thermophysical properties of metastable liquids have been very little studied. The viscosity of superheated liquids has only been measured at or near atmospheric pressure (600-1000 mm Hg) [1]. The difficulties involved in studying the properties of a superheated liquid are due to the fact that it only remains for a short period in the metastable state. This paper is devoted to the measurement of viscosity in a superheated liquid over wide temperature (20-200°C) and pressure (1.2-25 atm) ranges. The results may be used for expanding viscosity tables into the region of metastable states.

Experimental Apparatus and Measuring Technique

The viscosities of liquids in the metastable (superheated) state may be measured in a capillary visco-meter. The apparatus (Fig. 1) consists of devices for creating and releasing the pressure 12, a differential manometer 1, a glass capillary 7 (diameter ~ 0.08, length ~ 150 mm), and systems of automation and measuring instruments. During the experiments the test liquid remained at a pressure P_0 and flowed through the capillary 8 under the influence of a static pressure drop $(\rho_{Hg}-\rho)gh$ created by the mercury column h in the measuring tube 5 of the differential manometer. Here ρ_{Hg} and ρ are the densities of mercury and the test liquid at room temperature. The horizontally placed capillary was heated with a thermostated liquid (water, glycerin) pumped through the glass sleeve 9 from the thermostat 10. The remaining parts of the apparatus were at room temperature. The temperature of the liquid in the thermostat was kept constant to within ± 0.02°C even under the most difficult experimental conditions (at 200°C).

The flow of liquid through the capillary was not quite isothermal. The transitional region in which the
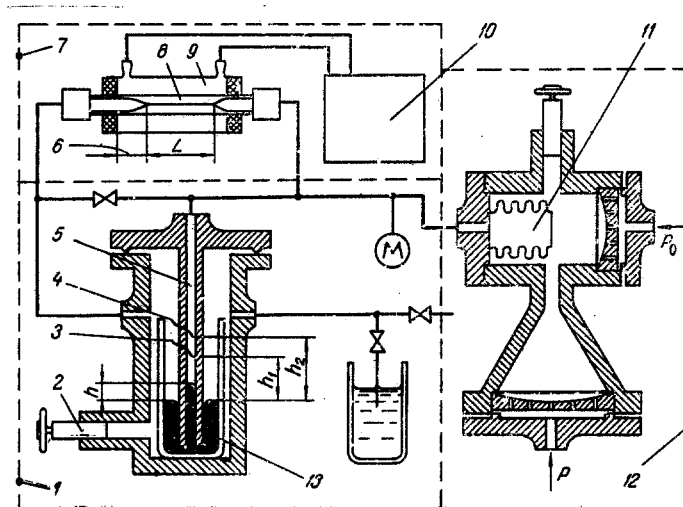
Fig. 1. Arrangement of experimental apparatus: 1) Differential manometer unit; 2) piston of differential manometer; 3, 4) lower and upper platinum contacts; 5) measuring tube of differential manometer; 6) preliminary liquid-heating section; 7) capillary unit; 8) capillary; 9) glass jacket; 10) thermostat; 11) bellows; 12) unit for creating and releasing the pressure; 13) mercury beaker.

liquid was heated while passing into the capillary increased in size with increasing thermostat temperature and pressure drop Δp. The extent of that part of the capillary in which the heating of the liquid took place was determined by calculation, using existing data relating to the isothermal and nonisothermal flow of a stable liquid. In order to reduce the deviation from isothermal conditions, a preliminary liquid-heating section 6 was provided (Fig. 1). This was made in the form of a wide glass tube sealed to the inlet end of the capillary. The ratio of the volume of the liquid in this section to the volume of the liquid in the capillary was approximately 200. Further increasing the volume of this section leads to an excessive shortening of the period spent by the liquid in the superheated state, so reducing the possibility of extending the measurements well into the metastable region.

The transition of the liquid into the metastable state was achieved by rapidly releasing the pressure from $P_0 > P_S$ to $P < P_S$. Liquid in the superheated state only passed into the capillary for the time necessary to make the measurements.

The viscosity measurements were made by a relative method. As reference values we took the viscosities of the test liquid in the stable region [2]. In these experiments we measured the time τ required for a specified volume of liquid $V = 0.25\pi d^2(h_2-h_1)$ to pass through the capillary under the action of a constant mean pressure drop $\Delta p = (\rho_{pT}-\rho)g(h_2-h_1)\ln(h_2/h_1)$. The measuring tube was made of Teflon. The distance between the platinum contacts was ~ 3 mm for $h_1 \approx 10$ mm. The system for creating and releasing the pressure was analogous to that used in bubble chambers [3] and also in experiments aimed at studying other properties of superheated liquids [4].

In order to create the pressure drop Δp the piston 2 in the differential manometer unit has to be moved. In this case the liquid passes through the capillary and measuring tube into the bellows 11. The level of the mercury in tube 5 is raised. The displacement of the piston is continued (by screwing in the threaded tail of the rod) until the mercury is lifted above the upper contact. The pressure-release mechanism (unit 12) operates immediately after the closing of the upper contact. After 0.2 sec the piston stops. During this period the mercury in the differential manometer tube has risen some 3 mm above the upper contact. After releasing the pressure, oscillations appear in the system; these die out completely in the time (1–5 sec) required for the mercury level to fall from its upper position until the contact 4 opens. A stopwatch measuring the time required for the liquid to pass through the capillary is started when the upper contact opens and stopped when the lower contact opens. After this the pressure is again raised to P_0.

The main operations — the creation of a difference in the mercury level, the release of the pressure, measurement of the time required for a specified volume of liquid to flow through, and restoration of the pressure to its original value — are carried out automatically.
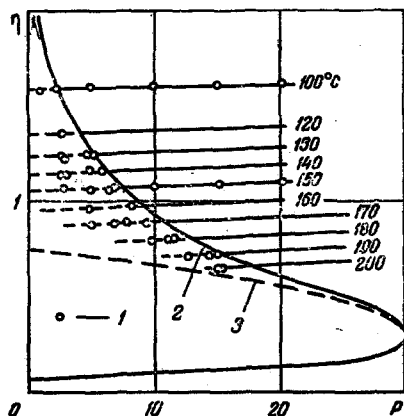
Fig. 2. Viscosity isotherms of n-hexane penetrating into the region of metastable states ($\eta \cdot 10^{-4}$ N·sec/m^2; P, bar). The continuous lines represent the data of [2] in the stable region; 1) our own data; 2) liquid−vapor equilibrium line [6]; 3) viscosity on the line of accessible superheating [4].

In processing the results of the measurements a correction was introduced for the nonisothermal nature of the flow. In order to determine the correction for the nonisothermal flow of the liquid through the capillary, special experiments were set up with a stable liquid at temperatures up to 150°C and pressures up to 20 bars. The nonisothermal nature of the flow was characterized by the ratio of the time τ required for the liquid to flow under the actual conditions of the experiment to the time τ_T required under isothermal conditions. The isothermal state was achieved by increasing the size of the preliminary liquid-heating section. The ratio τ/τ_T equalled 1.0 at room temperature and 1.15 at 150°C. In order to derive the computing formula the Poisseuille−Hagen law was employed; for the case of nonisothermal flow this may be written in the form

$$\Delta p = \frac{8 \int_0^L \eta_l dl}{\pi r^4 \tau} + m \frac{\rho V^2}{\pi^2 r^4 \tau^2}, \tag{1}$$

where r is the radius of the capillary, L is the length of the capillary (without allowing for the preliminary heating of the liquid) and $m \approx 1$.

According to the conditions of the experiment, when measuring the time required for the liquid to flow at a given temperature under two different pressures P and P_0 the value of Δp remains constant. Thus on equating the right-hand sides of Eq. (1) for these pressures (quantities with and without indices 0) we obtain

$$\left(\frac{8V \int \eta_{0l} dl}{\pi r^4 \tau_0} - \frac{8V \int \eta_l dl}{\pi r^4 \tau} \right) + m \left(\frac{\rho_0 V^2}{\pi^2 r^4 \tau^2} - \frac{\rho V^2}{\pi^2 r^4 \tau^2} \right) = 0.$$

An estimation of the quantities involved shows that the second term may be neglected by comparison with the first; we shall then have

$$\frac{\tau}{\tau_0} = \frac{\int \eta_l dl}{\int \eta_{0l} dl} = \frac{\int \left(\eta_{0l} + \frac{d\eta_{0l}}{dP} \Delta P \right) dl}{\int \eta_{0l} dl} = 1 + \left(\frac{1}{\eta_0} \cdot \frac{d\eta}{dP} - A \right) \Delta P$$

or

$$\frac{1}{\eta} \cdot \frac{d\eta}{dP} = \frac{\tau/\tau_0 - 1}{\Delta P} + A,$$

where

$$A = \int_0^L \left(\frac{\eta_{0l}}{\eta_0} \cdot \frac{d\eta}{dP} - \frac{d\eta_{0l}}{dP} \right) dl \Big/ \int_0^L \eta_{0l} dl \tag{2}$$

is the correction for the nonisothermal nature of the flow of liquid through the capillary $\Delta P = P - P_0$. The computing equation assumes the form

$$\eta = \eta_0 (\tau/\tau_0 + A\Delta P). \tag{3}$$

TABLE 1. Viscosity $(10^{-7} \ N \cdot sec/m^2)$ of N-Hexane as a Function
of Temperature and Pressure (bar)*

$T=100\ °C$, $P_s=2.46$ bars		$T=120\ °C$, $P_s=3.99$ bars		$T=130\ °C$ $P_s=4.97$ bars		$T=140\ °C$, $P_s=6.13$ bars		$T=150\ °C$, $P_s=7.47$ bars	
P	η	P	η	P	η	P	η	P	η
20,27	1630	20,27	1415	20,27	1290	20,27	1190	20,27	1111
15,20	1619	15,20	1395	15,20	1277	15,20	1177	15,20	1094
10,13	1605	10,13	1380	10,13	1263	10,13	1163	10,13	1084
5,07	1598	5,07	1360	5,07	1250	5,07	1170	6,89	1080
1,14	1570	2,74	1350	4,96	1250	4,96	1170	6,59	1070
—	—	2,63	1340	4,86	1250	4,86	1150	4,96	1070
—	—	—	—	2,94	1230	2,94	1140	2,84	1060
—	—	—	—	2,74	1240	2,74	1140	—	—

$T=160\ °C$, $P_s=9.04$ bars		$T=170\ °C$, $P_s=10.85$ bars		$T=180\ °C$, $P_s=12.94$ bars		$T=190\ °C$, $P_s=15.32$ bars		$T=200\ °C$, $P_s=18.02$ bars	
20,27	1010	25,33	930	25,33	845	25,33	765	25,33	687
15,20	993	20,27	918	20,27	833	20,27	748	20,27	665
10,13	975	15,20	905	15,20	820	15,20	730	15,20	643
8,82	984	9,49	895	11,65	811	14,39	721	15,0	655
4,96	972	7,90	891	11,15	809	12,77	714	—	—
—	—	6,89	888	9,93	802	—	—	—	—
—	—	5,17	881	—	—	—	—	—	—

* The states of the superheated liquid are distinguished by a stroke
lying below the latter.

The pressure dependece of A may be neglected, since the value of $d\eta/dP$ entering into the expression for A(2)
changes very little with pressure. This enables us to determine A experimentally for each temperature from
the results of measurements in the stable region under isothermal (τ_T) and nonisothermal (τ, τ_o) experimental
conditions:

$$A = \frac{\tau_T/\tau_{oT} - \tau/\tau_o}{\Delta P} \ . \tag{4}$$

The maximum value occurred at 200°C and equalled 0.0011 bar^{-1}. The time τ required for the liquid to flow
through was measured with an electric stopwatch of the PV-53L type having a scale division of 0.01 sec. The
time amounted to 6–50 sec, while the Reynolds number Re varied from 50 to 400, depending on the viscosity.
The flow through the capillary was always laminar. The pressure was measured with standard spring mano-
meters of class 0.2 having measuring ranges of 0–25 and 0–40 kgf/cm^2. The temperature was measured with
differential thermocouples (capillary walls) and mercury–glass thermometers (thermostat) having a scale
division of 0.1°C, verified by reference to a standard platinum resistance thermometer of the first category.

Results of the Experiments

The experiments were carried out with n-hexane of the chemically pure type. Before filling the apparatus,
the substance under test was redistilled and dried with CaCl$_2$ in the ordinary way [5], and also partly freed from
dissolved air by boiling in a flask with a reflux condenser.

The main error of the measurements is associated with the imprecise determination of A and the time
τ (random temperature fluctuations, variations in contact closing mode). The total error in the determination
of the viscosity for the maximum superheating is no greater than 1%. To this we must add the error with which
the viscosity values taken from [2] were determined.

Table 1 gives the results of our measurements of the viscosity of n-hexane, including a considerable pene-
tration into the region of superheated states. The states of the superheated liquid are distinguished by a stroke
(lying below the latter). We see from Fig. 2 that the points corresponding to the viscosity of the superheated
liquid lie (within the limits of experimental error) on the linear continuation of the isotherms into the region
of superheated states. This indicates the validity of our method of linearly extrapolating the isotherms from
the stable into the metastable region in order to derive information regarding the viscosity of the superheated
liquid. The results of this extrapolation coincide with experimental data obtained over the whole range studied:
$0.6 < T/T_C < 0.9$, $P_s - P \le 0.3(P_s - P_{su})$, where P_{su} is the pressure corresponding to the greatest possible
superheating of the liquid at the specified temperature [4], T_C is the critical temperature of the liquid.

If we assume that the viscosity isotherms retain their linearity for an even deeper penetration into the metastable region, we may approximate the viscosity for the states of accessible superheating of the liquids by the line 3 in Fig. 2. The region of metastable (superheated) states lies between lines 2 and 3.

NOTATION

ρ_{Hg}, ρ, densities of mercury at room temperature and the liquid under consideration at the thermostat temperature, respectively; g, gravitational acceleration; h, distance from the mercury level in the glass vessel to that in the measuring tube (Fig. 1); h_1, h_2, distances from the mercury level in the glass vessel to the lower and upper contacts, respectively; τ, time for a specified volume of liquid V to pass through the capillary V, V = $0.25 \pi d^2 (h_2 - h_1)$; d, internal diameter of the measuring tube; η, viscosity of the liquid under consideration; L, length; 2r, diameter of the capillary; A, a quantity allowing for the nonisothermal nature of the flow of liquid through the capillary; P_s, P_{su}, pressures of the saturated vapor and the greatest possible superheating of the liquid, respectively; T_C, critical temperature. Indices: 0, quantities corresponding to the reference pressure P_0.

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USE OF A MICROCALORIMETER OF THE CALVÉ TYPE
FOR DETERMINING THE KINETIC CHARACTERISTICS
OF THERMAL EFFECTS IN CHEMICALLY REACTING
MATERIALS

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The construction of a dynamic microcalorimeter designed for measuring the kinetic characteristics of thermal effects in solid and powdered polymer materials which react chemically on heating is considered.

It is well known [1] that the kinetic characteristics of thermal effects in chemically interacting materials may be determined calorimetrically from the relationship between the rate of heat evolution by unit mass of the reacting mixture $dQ/d\tau$ and the velocity $d\varphi/d\tau$ of the corresponding reaction. However, the adiabatic-microcalorimeter method usually employed has the following shortcomings: the necessity of introducing a correction for heat exchange with the ambient, and the impossibility of determining the thermal effect of the reaction without a priori knowledge as to the specific heat of the test material, which is assumed to be an invariant function with respect to temperature. The use of the dynamic microcalorimeter considered in this paper overcomes these obstacles and reveals the influence of heating rate on the kinetic parameters of chemically reacting materials.