AN APPARATUS FOR STUDY OF LIQUID SPECIFIC HEAT AT HIGH STATE PARAMETERS IN THE MONOTONIC HEATING REGIME

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Experimental apparatus is described and results of a study of thermal conductivity of n-heptane are presented.

Nonstationary methods, which have a number of advantages over stationary ones, are being ever more widely used to study the specific heat of liquids. The authors are aware of three studies which have used the monotonic heating method to measure specific heat C_p at high pressures [1-3]. In [1, 2] the quantity of heat absorbed by the liquid was determined by a heat meter. The liquid under study itself was used as the heat meter in [1], while [2] employed a gas layer. In both these cases a knowledge of the thermal conductivity of the heat meter material is necessary. However, data on thermal conductivity have uncertainties of more than 2%, which contributes directly to the uncertainty of the specific heat determinations. Moreover, in [1, 2] the accuracy required in measuring the thickness of the heat meter material layer was very high, and convective and radiant heat exchange were excluded. In [3] the amount of heat absorbed by the liquid was determined electrocalorimetrically; the heat meter used to monitor the adiabatic nature of the process was a thin layer of the liquid under study separated by a thin metal barrier from the device wall. The adiabatic condition was checked by simultaneous measurement of temperature on the barrier and the inner surface of the wall. However, in [3], just as in [1, 2], there were severe requirements on temperature uniformity in the metal barrier and the wall, which were difficult to satisfy at elevated temperatures.

In order to eliminate the above shortcomings, the present authors developed a device — an adiabatic calorimeter for direct heating of the specimen, which permits study of specific heat (C_p) of liquids by a rapid method over a wide parameter range.

The essence of the present method is the adiabatic heating of a fraction of the material under study with an internal heat source, while that mass is isolated from the remaining portion of the liquid by a heat meter mounted on the outer surface of the regulated heater. The specimen is located within a massive metal shell formed by a high-pressure autoclave, the temperature of which is increased monotonically. The adiabatic condition of the measurement cell is monitored by thermometers and controlled by adjusting the power level of the internal and adjustable heat sources. Figure 1 shows a schematic diagram of the calorimeter. The material under study is located within the massive metal shell 4, the temperature of which is increased monotonically. The material under study, within which there operates a thermal source 1 at power W, is surrounded by heat meter 2. On the outer surface of the heat meter is located a heat source 3 of power W_0. The thermal power of heater 1 is selected such that the temperature difference across the heat meter surfaces be as small as possible over the duration of the entire experiment and be zero in certain portions of the experiment.

Glass was used for the heat meter material, and the temperature difference across the heat meter was monitored by Chromel—Copel thermocouples. The glass heat meter permits accurate determination of the volume of the specimen studied and introduction of a correction for a nonadiabatic state, and is also convenient for thermocouple installation. Use of the thermocouple permits measurement of the integral temperature difference between the heat meter surfaces, so that one-dimensionality is no longer required in the temperature field, a condition which defined the upper temperature limit in [3]. The independence of the thermal conductivity coefficient of glass from the type of material introduced and the pressure makes possible the introduction of a correction for nonadiabatic conditions.

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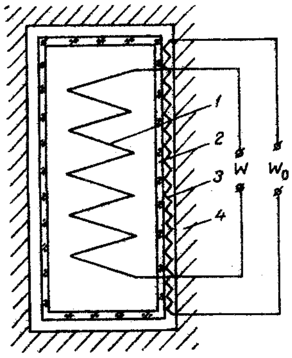

Fig. 1

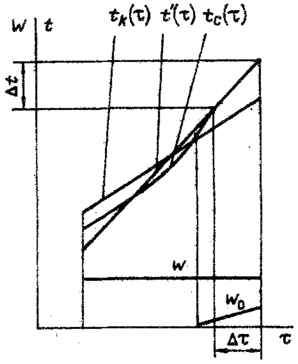

Fig. 2

Fig. 1. Schematic diagram of calorimeter.

Fig. 2. Heat meter surface and shell temperature.

Figure 2 shows sample curves of the temperature rise of the outer $t_c(\tau)$ and inner $t'(\tau)$ surfaces of the heat meter and the inner surface of the shell $t_k(\tau)$ with heat source 1 operating at a power W and heat source 3 with power level W_0.

In operation of a calorimeter of this type it is necessary to select the internal heat power such that the temperature of the inner heat meter surface $t'(\tau)$ be greater than the temperature of the outer surface. Then without changing the power level of the inner heater, one must adjust heater 3 to achieve the condition $t'(\tau) = t_c(\tau)$, then maintain this condition until the measurements are performed. By maintaining this condition, measuring the heating rate and amount of energy supplied, and using the geometric dimensions of the specimen, the volume heat capacity can be calculated.

The computation formula for true isobaric specific heat is derived from the condition of thermal balance of the calorimeter during continuous heating:

$$C_p = \frac{v}{V}\left(\frac{W-W'}{b} - C_1\right). \qquad (1)$$

The quantities C_1 and W' appearing in this expression are determined by special calibration experiments [4].

To measure specific heat C_p of a liquid at high pressures by this technique, a compact tabletop device was developed, and is shown schematically in Fig. 3. It consists of a glass ampul with thermocouples and a high-pressure shell.

The glass ampul (heat meter) has a cylindrical form, with inner diameter 18 mm, outer diameter 20.5 mm, and length of ≈150 mm. A Nichrome wire 0.15 mm in diameter with silicone insulation is mounted on the outer surface of the heat meter and contained within a shell 25 mm in diameter. Centering is accomplished by quartz rods.

Within the specimen under study there is located a spiral-shaped heater, made of 0.1-mm-diameter Nichrome wire, with a resistance of ≈230 Ω. The spiral diameter is such that the liquid volume inside and outside the spiral is approximately the same. The thermal power produced by this inner heater is determined by potentiometric measurements of the current and potential drop across the heater. The heater power supply is a "Volna" type battery.

A single-junction Chromel—Copel thermocouple is used to measure liquid temperature, and temperature difference between the heat meter walls is measured by a 100-junction Chromel—Copel thermocouple battery. Heat meter sensitivity is 0.972 W/mV, which makes possible monitoring of adiabatic conditions, reducing uncertainty in the specific heat determination to 0.2% [4].

Experimental temperature and heating rate are measured with a Chromel—Copel thermocouple, an R-363/1 potentiometer, and an S-11-1b stopwatch with 0.1-sec dial gradations. Temperature difference is monitored by an M 195/1 galvanometer.

The autoclave has one opening for installing the monitor thermometer and Chromel—Alumel thermocouple, while a high-pressure valve is located above, for convenience in filling and emptying the device.

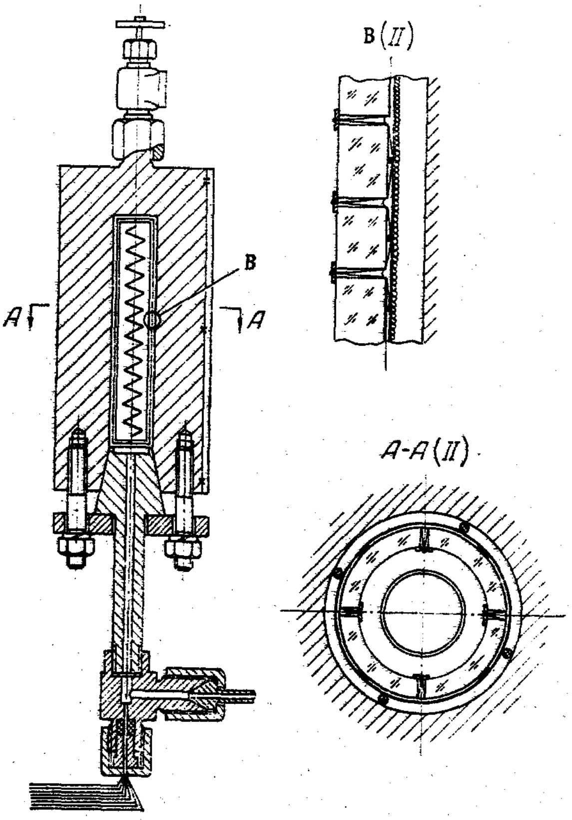

Fig. 3. High-pressure calorimeter.

An intermediate high-pressure vessel 4 (Fig. 4), 4 liters in volume, was used to create and maintain high-pressure conditions. The lower end of the vessel 4 is connected to the device 1 through reducer vessels 2 and an MP-600 hydraulic press 5, while the upper end is connected to a compressed air tank 6, with which pressures up to 140 bar are generated. Hydraulic press 5 is used for production of pressures above 140 bar. The intermediate vessel permits compensation of pressure nonuniformity and maintenance of constant pressure over the entire experiment.

The 600-bar reference manometer 3 and type MP-600 piston manometer 7 are used to measure pressure. Cone-type seals are used to ensure hermetic conditions, with measurement leads brought out through special seals. Four electric heaters are mounted on the outer surface of the autoclave: one main, one auxilliary, and two guard heaters.

Optimum voltages on the electric heaters are chosen beforehand in a series of control measurements. Temperature uniformity over autoclave length is monitored by two differential thermocouples, sealed into a groove in the outer surface. Temperature change along the autoclave length is measured by an M-95 galvanometer. Due to the high conductivity of the autoclave material (copper), the uniform placement of the heater, and the use of guard heaters, it was possible to reduce the temperature gradient along the measurement cylinder to a minimum not exceeding 0.7 deg K/m.

Experiments are conducted in the following order. After filling with the test substance (liquid) the calorimeter is connected to the high-pressure vessels. For degasification purposes the apparatus is heated to the liquid boiling point. The working pressure is generated by the high-pressure tank and hydraulic press. Then the liquid and autoclave body heater systems are switched on. Using a resistance box, the power level of the heater located inside the measurement cell is adjusted until the interior heat-meter temperature $t'(\tau)$ becomes greater than the outer temperature $t_c(\tau)$, after which a second resistance box is used to adjust the power level of the heater mounted on the outside surface of the heat meter to achieve the condition $t'(\tau) = t_c(\tau)$. Then the heating rate, current, and voltage of the inner heater are measured.

To measure the heating rate an emf is established with the R-363/1 potentiometer, somewhat higher than the thermocouple indication. As the galvanometer needle passes through the zero point, the stopwatch is turned on, then the potentiometer emf is increased and the stop-

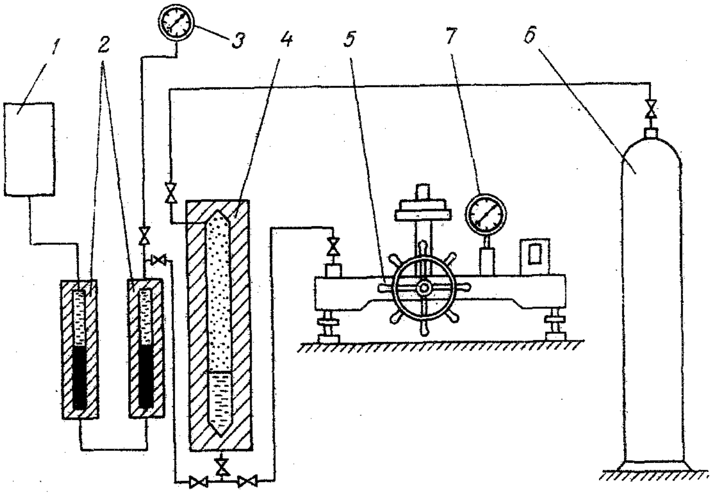

Fig. 4. Diagram of experimental high-pressure apparatus.

TABLE 1. Experimental Isobaric Specific Heat of n-Heptane, $C_p \cdot 10^{-3}$, J/kg·deg K

T, °K	P, MPa					
	0,1	5,0	10,0	20,0	30,0	50,0
303,16	2,2623	2,2505	2,2438	2,2308	2,2154	2,2092
323,16	2,3369	2,3236	2,3167	2,2990	2,2884	2,2772
343,16	2,4280	2,4139	2,4040	2,3829	2,3703	2,3565
363,16	2,5382	2,5184	2,5041	2,4789	2,4601	2,4438
383,16		2,6353	2,6150	2,5839	2,5569	2,5367
403,16		2,7631	2,7346	2,6953	2,6599	2,6329
423,16		2,9006	2,8609	2,8107	2,7682	2,7307
443,16		3,0469	2,9917	2,9281	2,8807	2,8288
463,16		3,2004	3,1248	3,0461	2,9961	2,9263
483,16		3,3592	3,2583	3,1633	3,1126	3,0241
503,16		3,5205	3,3903	3,2788	3,2282	3,1191
523,16		3,6802	3,5191	3,3922	3,3402	3,2150
553,16			3,7032	3,5576	3,4941	3,3609
573,16				3,6649	3,5812	3,4620

watch stopped the second time the needle passes the zero point. The heating rate is then determined from the emf's and the elapsed time.

Heating is carried on for periods of 3-4 h, depending on the value of the heating rate and the limiting experimental temperature.

Such a relatively low heating rate is intended to reduce to a minimum the nonuniformity in the temperature field and ensure that the process occurs in a strictly isobaric manner.

For a temperature of 293°K and atmospheric pressure the value $V = 35.16 \pm 0.06$ cm^3 was obtained. The confidence interval is given for a confidence coefficient $\alpha = 0.95$.

Analysis reveals that systematic error of the calorimeter does not exceed 1.0%.

The results of the study were processed with a Minsk-32 computer. To do this the functions $t = f(e)$, $C_1 = f(t)$, $W' = f(t)$, $v = f(P, t)$, $V = f(t)$ were first introduced into the machine memory, then the values of e_1, e_2, P, W_T obtained in experiment were entered as a data block, and the values of t, C_p, the functions $C_p = f(t)_{p=\mathrm{const}}$, $C_p = f(P)_{t=\mathrm{const}}$ were calculated, the latter being used to calculate C_p values for different temperature and pressure values. Results were then printed out.

The apparatus was used to study specific heat of n-heptane from room temperature to 583°K at pressures to 50 MPa in the liquid state.

The $v = f(P, t)$ values were taken from [5].

Smoothed data on n-heptane specific heat are presented in Table 1.

The maximum uncertainty in the experimental data does not exceed 1.4%.

Within the limits of experimental accuracy, the data obtained agree with those of [6] (at atmospheric pressure) and with calculated values obtained from the thermal equation.

NOTATION

C_p, isobaric specific heat, J/kg·deg K; v, specific volume of material studied, m^3/kg; V, volume of material studied heated by internal heat source, m^3; $b = \Delta t/\Delta\tau$, heating rate at specified temperature, deg K/sec; W, inner heater power, W; W', correction for thermal loss, W; C_1, ballast heat capacity of measurement cell at given temperature, J/deg K; e, emf; t, temperature °C; T, thermodynamic temperature, °K; R, universal gas constant, J/kg·deg K; P, pressure, MPa; τ, time, sec.

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APPARATUS AND METHOD TO DETERMINE THE ANISOTROPIC STATE OF ORIENTED POLYMER MATERIALS BY MEANS OF THERMOPHYSICAL PARAMETERS

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A method and apparatus are proposed for the determination of the heat-conduction anisotropy of oriented film materials. Experimental results on realization of the method are presented.

The technological processes to obtain film materials are related to the action of high temperature, pressure, and shear stress on polymer systems [1], which is accompanied by strain and orientation of the structural elements contributing to the origination of an anisotropic oriented state [2].

However, in a number of cases such a state results in obtaining oriented film materials with unstable physicomechanical properties and high shrinkage. These phenomena are associated with the incompleteness of the relaxation processes [3] in such systems and the origination of significant internal stresses [4].

In this connection, the development of methods to determine the degree of film orientation as a function of different technological factors is of great practical value.

The degree of polymer film orientation is usually estimated by the value of their birefringence [5] and by an acoustic method [6]. However, the results obtained by these methods do not always uniquely characterize the degree of orientation of the structural elements.

It is shown in this paper that a very promising method, which permits the determination of the degree of film material orientation as a function of different technological factors,

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