X, x, dimensionless and dimensional (m) space coordinates; α, heat-transfer coefficient $W/(m^2 \cdot K)$; δ, thickness of the coil insulation, m; λ, thermal conductivity of the insulation, $W/(m \cdot K)$; $\Theta = (T_w - T_{fin})/(T_{ini} - T_{fin})$, $\vartheta = (T_g - T_{fin})/(T_{ini} - T_{fw})$, dimensionless excess temperature of the wall and coolant, respectively; Π, heat transfer perimeter, m; $\phi(\tau)$, known time function; τ, time, sec; τ_b, balance time of cooling, sec; $St^* = \alpha \Pi L/(Gc_p)_g$ modified Stanton parameter. Subscripts: w, wall; g, coolant; p, at constant pressure; int, fin, initial and finite states, respectively; per, permissible; c, heat flux through the coil insulation; L, heat influx from the surrounding medium; max, maximum; ∞, cooling time of the spiral channel with a variable temperature of the coolant at the inlet.

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EXPERIMENTAL DEVICE FOR MEASUREMENT OF ISOBARIC SPECIFIC HEAT OF ELECTROLYTES AT HIGH STATE PARAMETERS

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UDC 536.2.083

Principles of operation and construction of an experimental device for measurement of isobaric specific heat of liquids (electrolytes) at high pressures are described.

The major shortcomings of existing calorimeters were pointed out in [1], which proposed a new pulse-regular method for simultaneous measurement of isobaric specific heat cp, thermal conductivity λ, and thermal diffusivity a of electrolytes. This method permitted measurements over wide ranges of temperature and pressure. In the present study this method is realized experimentally for measuring isobaric specific heat of liquids.

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 51, No. 5, pp. 789-795, November, 1986. Original article submitted September 17, 1985.

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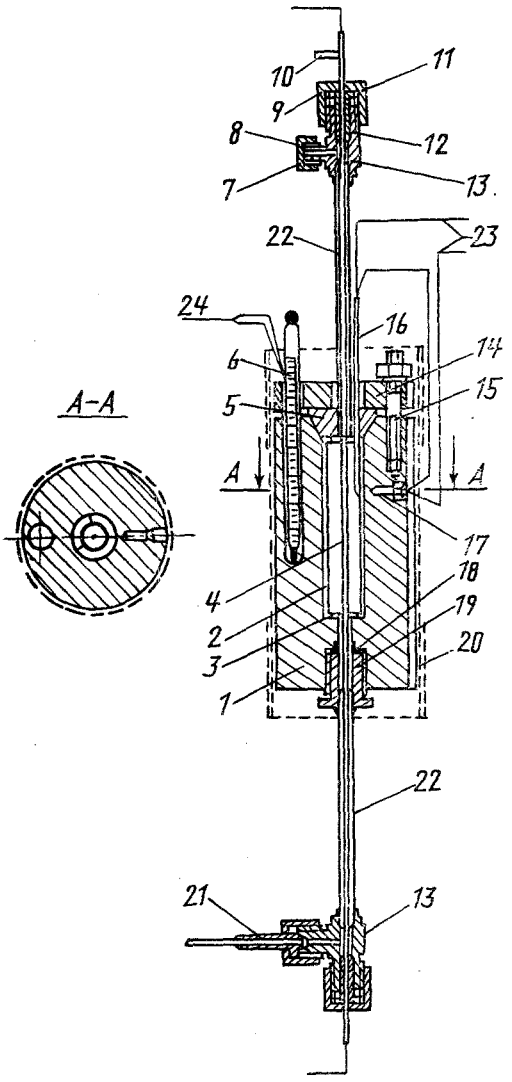

Fig. 1. Adiabatic high pressure calorimeter.

The experimental apparatus (Fig. 1) consists of a copper cylindrical body (the autoclave) 1 with internal diameter of 33 mm and external diameter of 106 mm. Within the copper body a thin wall copper cylinder (the ampul) 2 137 mm long, with outer diameter of 30 mm and inner diameter of 28 mm is mounted coaxially. Its ends are sealed with copper lids. A stainless steel capillary tube 4 (3 × 1.8) passes along the axis of cylinder 2. For electrical insulation purposes the heater is wrapped in glass fiber which was then impregnated with BF-2 resin and polymerized. The heater consists of a Nichrome wire 0.2 mm in diameter extending 137 mm along the capillary axis. This construction eliminates contact with the liquid under study. The annular gap between ampul and autoclave, 1.5 mm wide, is filled with the liquid to be studied and acts as a thermostat. To obtain a uniform annular gap width the ampul in which the liquid to be studied is located is centered within the autoclave by three quartz pins. The end gaps between ampul and autoclave are also controlled by three quartz pins 3 at each end.

The autoclave is hermetically sealed above by a stainless steel cone 5, which is held to the copper body by lid 14 and six pins 15, washers, and nuts. Two holes are drilled through the cone, one being in the center. A stainless-steel high-pressure tube 22 (8 × 4 mm) is welded to this hole to hold the capillary tube, while another capillary tube (housing) is welded to the other hole to hold one junction of the differential thermocouple 23. The housing is in intimate contact with the external surface of ampul 2.

A hole 17 is drilled through the lateral surface of the copper body to hold the second junction of the differential thermocouple. Another hole is drilled in the copper block to hold thermometer 6 and Chromel–Alumel thermocouple 24, used for visual observation and measurement of experimental temperature.

A stainless-steel probe 19 with high-pressure tube 22 connecting to the central capillary tube is screwed into the bottom of the body. A hermetic seal is insured by copper washer 18.

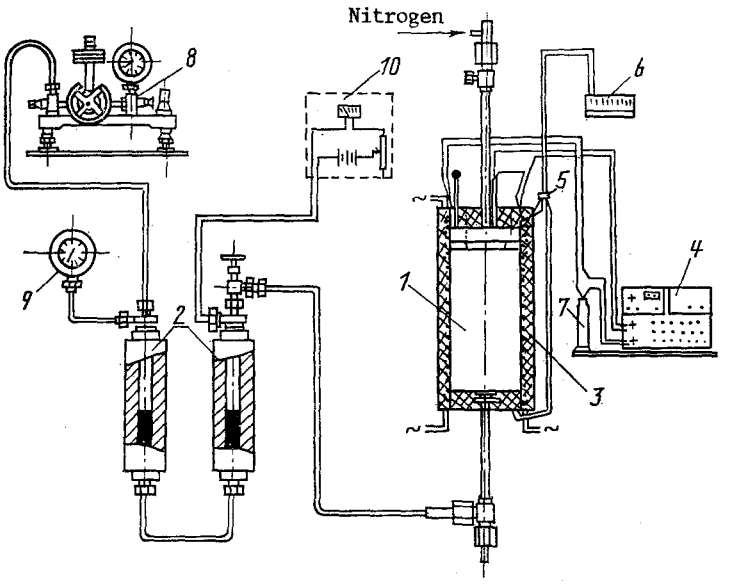

Fig. 2. Experimental high-pressure apparatus for measurement of liquid specific heat.

The tees 13 are welded to the high-pressure tubes 22 to allow filling and emptying the calorimeter and generating pressure. To produce pressure each tee contains pressure bushings (boxes) 11, Teflon washers 12, and end caps 9. The upper tee has a hole sealed by rubber washer 7 and end cap 8 for air exhaust during degasification and filling of the device with the liquid to be studied and connection to the high pressure vessels.

Nipple 10 is welded to the upper portion of the capillary tube for connection of the device to a Dewar flask with liquid nitrogen or to a vacuum pump. A gap 0.5 mm thick exists between capillary 4 and high pressure tube 22, which is needed for filling and emptying the device.

The 0.2 mm Chromel–Alumel thermocouples used were electrically insulated by wrapping them in glass fiber impregnated with BF-2 resin with subsequent polymerization.

The temperature regime in the high-pressure calorimeter is created by thermostatic furnace 20, the shell of which is made of sheet iron. The furnace contains three heaters; one main and two guard heaters. It is driven from the power line through S-0.75 and LATRy-1M voltage regulators.

Experiments are performed as follows: After filling with the liquid to be studied the calorimeter 1 (Fig. 2) is connected to high-pressure vessel 2. For degasification, the liquid is heated to its boiling point, after which the device is hermetically sealed. Furnace 3 is used to create a steady-state thermal regime in which the temperatures of the liquid and the copper body equalize (the galvanometer of the type R-363-2 potentiometer 4 indicates a null). Then using the liquid nitrogen equipment described in [2] nitrogen is fed to the calorimeter through the capillary tube. The nitrogen (gaseous), passing through the capillary tube in which the inner heater is located, cools the liquid-filled ampul. As compared to the temperature of the body, the temperature of the ampul rapidly decreases by approximately 0.5-0.7°K, or several decades of galvanometer scale divisions. Then the nitrogen supply is terminated, and the internal heater passing along the capillary axis is immediately turned on. The ampul is heated by 0.7-1.0°K, the galvanometer needle returns to its former position at a variable rate by a regular regime law. As the galvanometer needle crosses the −10 scale mark a ChZ-34 electronic stop watch is activated, and then switched off when the needle crosses the +10 scale mark, i.e., the ampul heating rate is measured in the vicinity of zero temperature difference, in a close to adiabatic state. The markings (−10) and (+10) correspond to (−0.14285) and (+0.14285)°K. Each experimental point is measured 2-3 times.

A groove is milled into the side of the copper calorimeter body to hold two differential thermocouples 5, which are used to monitor the uniformity of the temperature distribution over the length of the autoclave (a type M 195/1 galvanometer 6 is used to take the readings).

TABLE 1. Experimental Measurement Results

T, K	P, MPa															
	0,1		2,5		5		10		20		30		40		50	
	c_p	c_p'	c_p	c_p'	c_p	c_p'	c_p	c_p'	c_p	c_p'	c_p	c_p'	c_p	c_p'	c_p	c_p'
Water																
318,65	4,177	4134,8	4,171	4133,5	4,164	4132,1	4,153	4130,1	4,132	4126,0	4,112	4122,01	4,091	4117,6	4,07	4113,38
343,15	4,198	4104,82	4,184	4094,5	4,1704	4087,0	4,1577	4083,0	4,135	4077,9	4,114	4074,0	4,093	4069,8	4,072	4065,48
364,15	4,2185	4069,17	4,209	4059,0	4,19	4050,5	4,1776	4045,0	4,148	4037,0	4,124	4030,5	4,1004	4024,5	4,078	4018,5
388,65	—	—	4,242	4020,0	4,232	4015,8	4,204	3998,0	4,176	3989,9	4,148	3982,0	4,123	3975,0	4,0955	3968,5
414,45	—	—	4,298	3978,0	4,2716	3961,5	4,252	3951,5	4,221	3942,5	4,1896	3934,0	4,158	3925,3	4,127	3917,0
457,55	—	—	4,43	3911,8	4,398	3891,5	4,365	3875,99	4,309	3854,0	4,27	3843,0	4,237	3838,5	4,205	3832,64
494,15	—	—	4,627	3882,05	4,591	3862,5	4,537	3833,8	4,457	3803,16	4,4	3788,4	4,348	3775,0	4,3	3760,35
Benzol																
322,05	1,7915	1518,26	1,784	1516,4	1,7765	1517,1	1,77	1519,0	1,766	1529,2	1,762	1539,1	1,759	1548,9	1,756	1560,7
351,15	1,925	1570,8	1,909	1561,56	1,8978	1559,56	1,88	1555,7	1,8746	1569,95	1,87	1584,83	1,867	1600,03	1,864	1615,1
376,45	—	—	2,0194	1596,0	2,006	1593,36	1,987	1588,6	1,9755	1603,3	1,967	1621,79	1,964	1637,6	1,960	1652,6
423,55	—	—	2,237	1640,4	2,21	1634,3	2,18	1632,82	2,1505	1646,23	2,136	1665,04	2,128	1683,21	2,121	1701,4
449,65	—	—	2,36	1647,28	2,33	1644,98	2,29	1643,075	2,249	1659,76	2,227	1681,27	2,219	1704,03	2,210	1725,5
473,55	—	—	2,49	1645,9	2,438	1638,34	2,375	1631,63	2,32	1651,16	2,29	1678,57	2,279	1703,4	2,27	1729,5
498,35	—	—	—	—	2,53	1598,96	2,45	1602,3	2,38	1628,5	2,34	1655,5	2,314	1680,04	2,302	1705,1
n-Butyl alcohol																
321,05	2,5934	2038,41	2,583	2039,28	2,575	2039,92	2,5648	2040,3	2,5519	2050,2	2,55	2064,99	2,546	2076,52	2,541	2089,46
349,20	2,843	2170,3	2,83	2163,0	2,82	2165,01	2,81	2166,5	2,803	2184,05	2,793	2201,95	2,786	2216,01	2,779	2233,2
373,35	3,085	2286,91	3,0482	2270,29	3,039	2272,58	3,019	2273,13	3,006	2293,405	2,9953	2311,49	2,9911	2333,08	2,9902	2353,3
399,15	—	—	3,2776	2353,37	3,255	2350,11	3,237	2355,06	3,223	2384,96	3,2098	2412,48	3,2026	2432,39	3,1853	2447,93
421,75	—	—	3,461	2398,47	3,445	2404,61	3,4278	2418,16	3,3935	2441,64	3,369	2464,42	3,357	2487,67	3,346	2509,4
448,55	—	—	3,726	2462,5	3,696	2461,54	3,663	2474,36	3,62	2506,85	3,5805	2533,2	3,5602	2558,0	3,537	2580,5
472,95	—	—	4,01	2506,25	3,945	2495,21	3,89	2510,99	3,8144	2544,22	3,7614	2569,03	3,7305	2598,28	3,702	2624,76
522,15	—	—	—	—	4,39	2399,14	4,277	2459,23	4,136	2523,08	4,064	2574,4	3,994	2601,79	3,948	2631,08

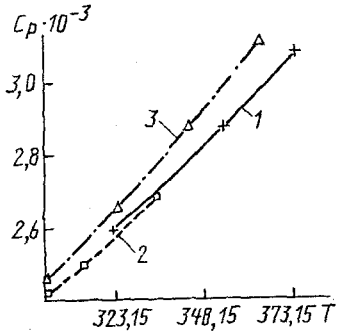

Fig. 3

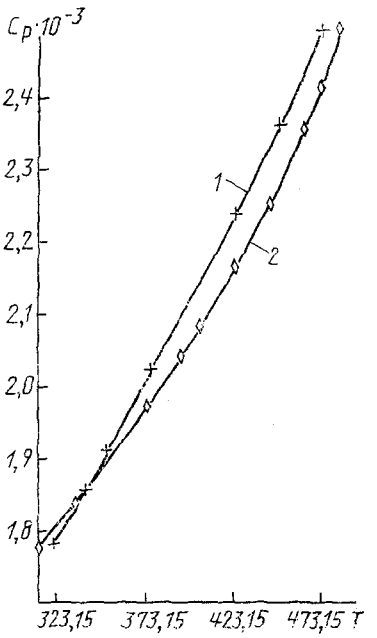

Fig. 4

Fig. 3. Comparison of data on specific heat of n-butyl alcohol at atmospheric pressure: 1) present data; 2) [7]; 3) [6]. T, °K.

Fig. 4. Comparison of data on specific heat of benzol at 2.5 MPa: 1) present data; 2) [5].

The experimental temperature is measured by a Chromel–Alumel thermocouple, the cold junction of which is located in a thermos bottle 7 filled with ice and an R-363-2 self-calibrating semiautomatic potentiometer of accuracy class 0.002. The thermocouples were precalibrated against a PTS-10 platinum resistance reference thermometer with accuracy of 0.02-0.3°K.

The experimental pressure was generated and measured by an MP-600 loaded piston manometer 8 of accuracy class 0.05 and a reference manometer 9 of accuracy class 0.35.

The piston manometer is connected to the calorimeter through two intermediate vessels 2, which are half filled with mercury. The mercury level in these vessels is monitored by an electrical circuit 10, fed from a dc power supply.

Calculations show that in the present case in the annular layer of material the quantity GrPr < 1000. Many scholars feel that in such a case convection will be absent. However, for a vertically oriented measurement cell, convection may still occur down to a low value of the Rayleigh criterion [3]. It is true that the effect of convective heat transport on thermal conductivity through the annular layer for the nonsteady-state method of measurement should obviously be lower [3]. This effect must be considered when determining the thermal conductivity and diffusivity coefficients.

In the present study only isobaric specific heat was measured, and the conductivity of the layer does not enter the computation formula, but serves only to monitor the achievement of an adiabatic state in the ampul during the temperature change process. Therefore the presence of weak convection in the liquid layer will play no role in measurement of specific heat.

To calculate the volume (isobaric) specific heat the computation equation obtained in [1] was used:

$$c_p' = \frac{1}{V'}\left(\frac{W - W_{\text{loss}}}{b} - M_b c_b\right), \tag{1}$$

where

$$V' = V\left(1 + \frac{2\delta}{3R_1} + \frac{2\delta'}{3l}\right). \tag{2}$$

To find the mass specific heat the well-known relationship $c_p = c_p'/\rho$ was used. The quantity $M_b c_b$ is found by calculation.

In experiment the ampul heating rate is measured as it passes through the adiabatic state; V' is calculated from the geometric dimensions of the measurement cell with consideration of their dependence on temperature; W is measured by a type D592 high-accuracy wattmeter; W_{loss} is determined from calibration experiments using water at atmospheric pressure.

To test the capabilities of the device, control measurements of c'_p of water and benzol were performed, together with the main studies of c'_p of n-butyl alcohol at temperatures of 318.65-522.15°K and pressures of 0.1-50 MPa (Table 1). The experiments used distilled water, benzol, and chemically pure grade n-butyl alcohol with the following characteristics; benzol, ρ_4^{20} = 880.0 kg/m³, n_d = 1.5015; T_b = 353.25°K; T_f = 278.683°K; n-butyl alcohol, ρ_4^{20} = 809.5 kg/m³, n_d = 1.3925, T_b = 390.65°K, T_f = 183.15°K.

Since the literature does not provide data on c'_p, values were calculated for the liquids (water, benzol, n-butyl alcohol) on the basis of values of c_p [4-7] and density [5, 8, 9] presented in the literature. Then the values obtained were compared to those obtained experimentally. Results of the comparison for water were quite good, with the maximum deviation being ±1.1%.

It is evident from Fig. 3 that the present data on specific heat of n-butyl alcohol at atmospheric pressure agree satisfactorily with the data of [6, 7]: the data of [6] are no more than 3.6% higher, while those of [7] are no more than 1.0% lower than the present data. At high pressures and temperatures the data of [7] on isobaric specific heat of n-butyl alcohol diverge more from the present values: at high temperatures they are somewhat higher than the present study at 2.5-10 MPa, and somewhat lower at 20-50 MPa.

As is evident from Fig. 4, the divergence of the present data on isobaric specific heat of benzol at 2.5 MPa from the data of [5] ([5] contains no data for atmospheric pressure) does not exceed 3.7%. At high temperature and pressure the divergence increases to 4%.

An analysis of all possible error sources indicates the uncertainty of the volume specific heat measurements to be ±2%.

NOTATION

c'_p, volume isobaric specific heat, J/(m³·K); c_p, isobaric specific heat, J/(kg·K); ρ, density of the test substance kg/m³; V, volume of material in ampul, m³; $b = \Delta t/\Delta\tau$, heating rate at given temperature, K/sec; W, internal heater power, W; W_{loss}, correction for thermal power losses, W; $M_b c_b$, ballast heat capacity of ampul, J/K; δ, δ', thickness of annular and endplane liquid layers, m; R_1, ℓ, radius and length of ampul, m.

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