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DETERMINATION OF THERMOPHYSICAL CHARACTERISTICS OF MULTICOMPONENT LIQUIDS

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UDC 536.63:536.711

A new approach is developed for determining the specific isobaric heat capacity and thermal expansion coefficient of multicomponent liquids.

Modern techniques of measuring heat capacity are based on the calorimetric method or a method depending on the unique features of sound or ultrasound propagation through the liquid under study [1-5]. For well-known reasons neither of these methods permits determination of the heat capacity of multicomponent "coarse" liquids such as heavy petroleum, suspensions, solutions, etc. with sufficient accuracy. At the present time no methods are known for determination of c_p of such liquids over wide ranges of temperature and pressure, especially at high pressures.

We will consider the possibility of determining the isobaric specific heat of multicomponent liquids commencing from the fact that with adiabatic increase (or decrease) in pressure in a thermostatted liquid-filled vessel there will be a corresponding increase (or decrease) in temperature of the liquid, characterized, in particular, by its specific heat.

The change in liquid temperature under adiabatic compression (or expansion) can be determined theoretically from the thermodynamic relationship [6]

$$\frac{1}{V} T dS = c_p dT - T \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P dP. \quad (1)$$

Considering that for a reversible adiabatic process the change in entropy dS is equal to zero, and taking $1/V(\partial V/\partial T)_P$ constant, for a finite pressure change we obtain the following expression for specific (per unit volume) isobaric heat capacity:

$$c_p = \frac{\alpha_P (P - P_0)}{\ln(T/T_0)}, \quad (2)$$

where T_0 , P_0 and T , P are the initial and final temperature and pressure; $\alpha_P = 1/V(\partial V/\partial T)_P$ is the thermal expansion coefficient at constant pressure. It is insured that the process occurs adiabatically by changing the pressure at a rate such that heat exchange between the system under consideration (thermosensor-liquid shell) and the surrounding thermodynamic medium does not have time to develop.

It has been shown experimentally [7] that the dependence of the temperature change ΔT of a liquid under compression or expansion on the rate of pressure change $\Delta P/\Delta \tau$ is of an exponential nature. Data from experiments with the apparatus to be described below were used to construct $\Delta T = f(\Delta P/\Delta \tau)$ for various liquids at $\Delta P = 10$ MPa (Fig. 1). It is evident that for each liquid the value of $(\Delta P/\Delta \tau)_a$ at which the process can be considered adiabatic differs. We note that of the liquids considered the required rate is highest for kerosene.

The value of $(\Delta P/\Delta \tau)_a$ is related to the heat-exchange properties of both the liquid itself, and the container within which it is located. Moreover, experimental results have shown that $(\Delta P/\Delta \tau)_a$ depends linearly upon the value of the pressure change ΔP . Thus, for example, for kerosene at $\Delta P = 10$ MPa $(\Delta P/\Delta \tau)_a = 1$ MPa/sec, at $\Delta P = 1$ MPa the value of $(\Delta P/\Delta \tau)_a$ is ten times smaller, 0.1 MPa/sec. Thus there exists a certain definite adiabatic pres-

M. Azizbekov Azerbaidzhan Petroleum and Chemistry Institute, Baku. Translated from *Inzhenerno-Fizicheskiy Zhurnal*, Vol. 47, No. 2, pp. 262-267, August, 1984. Original article submitted March 14, 1983.

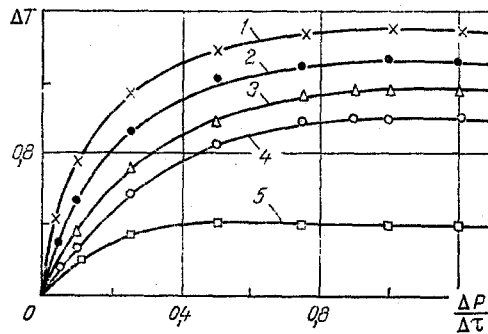


Fig. 1. Change in temperature ΔT ($^{\circ}\text{K}$) versus rate of pressure change $\Delta P/\Delta \tau$ (MPa/sec) at $\Delta P = 10$ MPa: 1) kerosene; 2) petroleum ($\rho = 855 \text{ kg/m}^3$); 3) transformer oil; 4) petroleum + 30% tar ($\rho = 900 \text{ kg/m}^3$); 5) clay solution.

sure change time $\Delta \tau_a$ (for kerosene ~ 10 sec), over the course of which the wall temperature has no marked effect on the liquid temperature in the direct vicinity of the thermosensor. We note that with increase in container diameter the value of $\Delta \tau_a$ increases.

The process under consideration occurs practically in equilibrium, since experiments with forward and reverse pressure changes revealed no residual phenomena and the temperature curves for the two cases coincided.

Figure 2 shows a view of the experimental equipment, which consists of a thermostatic high-pressure vessel 1 with inner diameter 38 mm, drive rod 2, which is moved by rotating flywheel 3 with crank 4, thermosensor 5 at the center of the vessel, reference manometer 6, and stand 7. The thermosensor used was an 0.1-mm-diameter Chromel-Copel thermocouple.

Determination of c_p with this apparatus is a simple process: the pressure in the thermostatic vessel is increased or decreased by moving the rod, ensuring adiabatic conditions, and the reference manometer and an R-363/1 potentiometer connected to the thermocouple are used to determine the corresponding temperature and pressure changes. The values of ΔP , T_0 , and T with known αp are then used with Eq. (2) to calculate c_p . We note that it is not necessary to produce any specific value of ΔP : the crank is turned to produce some arbitrary pressure change up to 1 MPa and the corresponding temperature change is measured.

This method of measuring isobaric heat capacity is characterized by a small number of parameters to be measured, simplicity of required equipment, and rapidity in performance of the measurement, which is of special importance for determining c_p of multicomponent liquids with unstable structural properties. It should also be noted that heat capacity of multicomponent liquids can be determined at practically all possible temperatures and pressures. Experiments performed with reference liquids have shown (Table 1) that the experimental c_p values differ from corresponding reference book values by not more than 4.8%.

It is obvious that the accuracy of the thermal conductivity determination is essentially determined by the quality of the pressure and temperature measurements. It can be expected that further refinements in measurement technique will improve the accuracy of c_p measurements by this method.

Experimental results on isobaric heat capacity of multicomponent liquids are presented in Table 2.

In those cases where the thermal expansion coefficient αp for the liquid is not known beforehand, it can be determined very simply with this apparatus, no additional equipment being required.

To determine αp we make use of the process of equalization of temperature of the liquid under study to the thermostat temperature, which occurs after adiabatic pressure change. To do this, we ensure pressure constancy by moving the bar, and measure the change in liquid volume (ΔV_1) as a function of temperature with the aid of scale 8, indicator 9, attached to the drivebar, and subscale attached to the rim of the flywheel with fixed indicator 10. Then αp is found from the expression

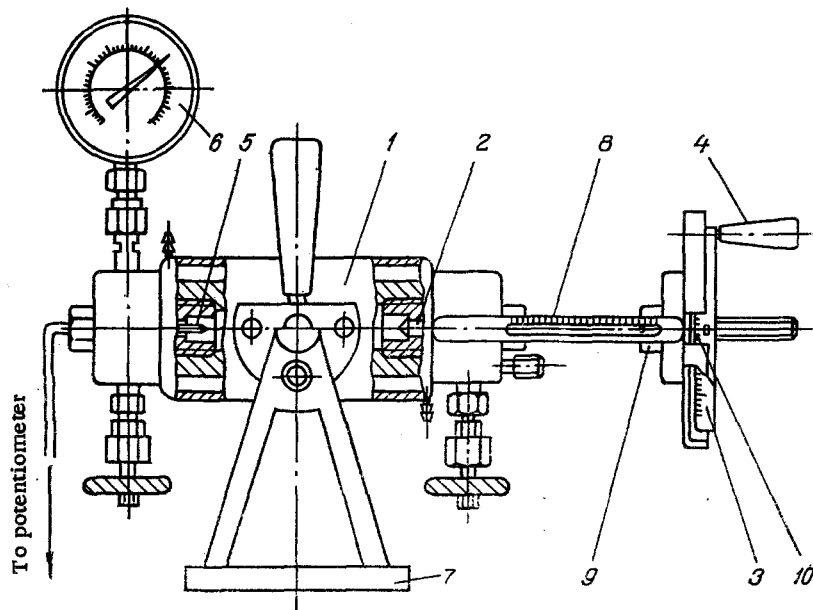


Fig. 2. View of equipment for c_p determination.

TABLE 1. Experimental c_p Values ($\text{kJ/m}^3 \cdot \text{deg K}$) of Reference Liquids ($\Delta P = 1 \text{ MPa}$, $P_0 = 0.1 \text{ MPa}$)

Liquid	$T_0, ^\circ\text{K}$	$\rho_0, \text{kg/m}^3$	$\alpha_p \cdot 10^3, 1/\text{K}$	$\Delta T, \text{K}$			$c_p \cdot 10^{-3}$		
				calc.	exptl.	uncertainty, %	ref. value	expt.	uncertainty, %
Hexane	293.15	659.4[10]	1.396[10]	0.276	0.286	3.5	1.482[10]	1.432	3.4
Distilled water	293.15	998.5[11]	0.2067[11]	0.0144	0.0152	5.2	4.177[13]	3.975	4.8
Benzol	311.55	859.5[12]	1.2637[10]	0.2555	0.252	1.4	1.518[12]	1.562	2.9

$$\alpha_p = \frac{1}{V_0} \left(\frac{\Delta V_1}{\Delta T} \right)_p$$

Values of α_p found for a number of liquids by this technique are presented in Table 2. The maximum uncertainty does not exceed 2%.

The technique of [8] was used to estimate the accuracy of c_p determination from the uncertainties of the quantities appearing in Eq. (2):

$$\delta(c_p) = \sqrt{\left[\frac{\Delta(\alpha_p)}{\alpha_p} \right]^2 + \left[\frac{\Delta(\Delta P)}{\Delta P} \right]^2 + \left[\frac{\Delta\varphi(T)}{\varphi(T)} \right]^2},$$

where $\varphi(T) = \ln(T/T_0) = \ln(1 + \Delta T/T_0)$.

With consideration of the maximum divergence (5.2%) found in Table 1 between calculated and experimental ΔT values, as well as the uncertainty in measurement of the temperature T_0 (0.01%), as determined by the technique of (9), $\Delta\varphi(T)/\varphi(T) = 4.8\%$.

On the basis of [10-12], for the thermal expansion coefficient we have $\Delta(\alpha_p)/\alpha_p = 1.31\%$. For the liquids listed in Table 1 this value considers the maximum error (1.25%) related to the assumption that $\alpha_p = \text{const}$ over the pressure change range $\Delta P = 1 \text{ MPa}$, as well as the uncertainty in α_p determination (0.06%).

When pressure is measured by a class 0.35 accuracy reference manometer $\Delta(\Delta P)/\Delta P = 0.7\%$.

Thus, the maximum uncertainty in c_p determination by the technique described at $\Delta P = 1 \text{ MPa}$ does not exceed 5%. If we consider the experimental uncertainty of α_p determination (2%), then the maximum uncertainty in c_p determination is 5.3%.

In choosing a ΔP value it must be kept in mind that with increase in ΔP the value of c_p then refers to a greater pressure range. On the other hand, with decrease in ΔP the corre-

TABLE 2. Experimental c_p Values ($\text{kJ/m}^3 \cdot \text{deg K}$) of Multicomponent Liquids ($P - P_0 = 1 \text{ MPa}$, $T_0 = 311.4^\circ\text{K}$, $P_0 = 1 \text{ MPa}$)

Liquid	$c_p \cdot 10^{-3}, \text{ J/K}$	$\rho, \text{ kg/m}^3$	$\Delta T, \text{ K}$	$c_p \cdot 10^{-3}$
Condensate	1.215	755.6	0.241	1.540
Petroleum	0.742	855.0	0.132	1.712
Petroleum (30% tar)	0.701	930.0	0.099	2.160
Clay solution	0.479	1090	0.338	3.838
Solution of polyacrylamide in water (0.6%)	0.448	995	0.42	4.337
Solution of polyisobutylene in petroleum (26.7%)	0.711	845	0.133	1.632

sponding temperature change also decreases, and in measurements performed below a certain value of ΔP the uncertainty related to temperature determination increases significantly. In connection with this, with the equipment used in this study the most suitable value of ΔP lies in the range 0.1-1 MPa.

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