NEW METHOD FOR DETERMINATION OF THERMOPHYSICAL PROPERTY COMPLEXES OF LIQUIDS AT HIGH STATE PARAMETERS

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A high-speed nonsteady-state method for measurement of thermophysical properties of liquids at high state parameters is developed.

Several methods are known for the measurement of specific heat [1-4] and thermal conductivity [1, 5] of liquids at high pressure in the monotonic heating regime, the fundamentals of which are described in [6]. These methods have been employed to measure the thermal conductivity and specific heat of various classes of liquids at high pressures and temperatures. However, together with their well-known advantages, those methods possess a number of shortcomings.

In [1, 2], to determine the specific heat c_p the amount of heat absorbed by the liquid was determined by a heat meter (measuring the liquid under study or air). Then to calculate c_p it was necessary to know the thermal conductivity coefficient of the heat meter material. However, available thermal conductivity data have an uncertainty of more than 2%, which is introduced into the specific heat measurement. Moreover, the high ballast heat capacity of the calorimeter has a negative effect on experimental accuracy [2]. Because of this impulse-dynamic methods were then used [3, 4]; an adiabatic calorimeter with direct continuous heating of the specimen eliminated the shortcomings mentioned above.

However, the c-calorimeter and λ-calorimeter used with the monotonic heating method, still have shortcomings, namely:

1. Severe Requirements as to Uniformity of the Temperature Field on the Surfaces of the Core and Shell, Which Are Impossible to Achieve with External Heating of the Autoclave. Furthermore, with increase in autoclave temperature this nonuniformity increases. Thus, experiments have shown that at t = 200°C for a copper autoclave the nonuniformity may be as high as 0.5°. Since the nonuniformity depends on the state of the external calorimeter isolation, the temperature gradient along the autoclave, the material and dimensions of conducting wires and high-pressure tubes for the thermocouples, etc., its theoretical calculation is difficult.

To generate a mean value of temperature difference experimentally, [4] used a 100-junction thermobattery, which complicated the construction of the measurement cell.

2. Impossibility of Repeating Individual Experimental Points Which Originally Appeared Unreliable to the Experimenter. Since the method is dynamic, the experimental temperature must change with time. To obtain a desired state in the material, the experiment must be repeated from the beginning.

3. Necessity of Introducing into the Computation Equation Corrections for Variability of the Heating Rate and Physical Properties of the Liquid. With poor autoclave insulation and high temperatures such corrections can be significant.

4. The Impossibility of Determining the Entire Complex of Thermophysical Properties from Data of a Single Experiment. In [1] a two-cell device of complex construction was proposed for simultaneous measurement of the thermal conductivity coefficient and the specific heat (c_p).

5. The Necessity of Maintaining Constant Pressure in the Vessel over the Course of the Entire Experiment to Obtain Isobaric Specific Heat. In [1] constancy of pressure was achieved by inclusion of a buffer volume and high pressure gas reservoir in the hydraulic

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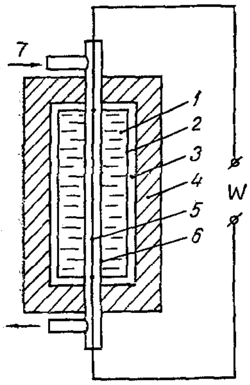

Fig. 1. Schematic diagram of calorimeter.

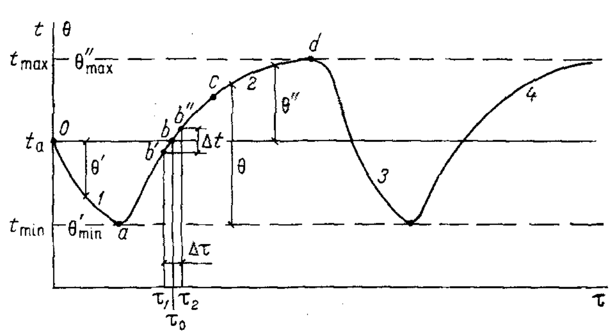

Fig. 2. Measurement cell temperature vs time.

system, while [3] achieved this result by automatic pressure regulation in the hydraulic press.

6. Necessity of Determining Thermmeter Temperature Difference to a High Accuracy. At low values of this difference the problem becomes more complicated.

7. The High Value of the Initial Nonsteady-State of the Thermal Regime, Sometimes Reaching 30-50°. This does not permit testing of the apparatus at room temperature, at which the state of the device is more uniform and subject to control.

8. The Possibility of Change in the Chemical Structure of Some Organic Liquids (for example, olefins) Due to Multiple Heating to the Maximum Experimental Temperature and Cooling to the Minimum Temperature.

To eliminate these shortcomings we propose an impulsive-regular regime method, which permits determination of specific heat c_p, thermal conductivity, and thermal diffusivity of liquids (including electrolytes) at high pressures and temperatures.

Figure 1 shows a schematic diagram of the calorimeter. The liquid to be studied 1 is located within a thin metallic shell 2 (the ampul), the temperature of which is changed during the course of the experiment. The shell is surrounded by a thin layer 3 (heat meter) of the liquid under study, contained in a massive metallic high pressure autoclave 4. Along the axis of the ampul is the heat source 5, generating power W, separated from the liquid by a thin metallic high pressure tube 6. When necessary cold atmospheric air or liquid nitrogen 7 can be passed along the tube to cool the ampul.

Measurements are performed in the following manner. A steady state thermal regime is established in the autoclave at the experimental temperature and pressure. Cold air is passed through the tube (3 × 1.8 mm) (if the autoclave temperature is high), or liquid nitrogen may be used (if the autoclave is at a moderate temperature). The ampul temperature t then decreases to some temperature head $\theta' = t_a - t$ as compared to the autoclave temperature (Fig. 2). One can say that the temperature decrease occurs along the exponential curve 1. The maximum value of θ' is approximately 0.5-1.0°. Then the coolant supply is terminated, and an electrical heater (wire 0.2 mm in diameter) supplying a constant power W = const (2-4 W dependent on liquid properties) is switched on at the same time. The ampul temperature increases along curve 2, asymptotically approaching $\theta''_{max} = t_{max} - t_a$, the maximum ampul temperature head (approximately 0.5-1.0°). With the exception of a short lower segment curve 2 follows a strictly specific law, which we may term the heating rate m. The temperature curve may be repeated (curves 3, 4, etc.) if necessary.

Determination of the isobaric specific heat, thermal conductivity coefficient, and thermal diffusivity then reduce to measurement of the heating rate at points b and c of heating curve 2.

We will now derive a computation equation for determining the thermophysical properties of the liquid. To derive the relationships for specific heat c_p we first assume: 1) the specific heat (overall) of the autoclave is extremely high, and remains constant over the time of the experiment; 2) there is no temperature head across the dividing surfaces of the measurement cell; 3) there is no heat loss along wires and tubes; 4) the liquid layer thickness is significantly less than the diameter of the ampul; 5) the ballast heat capacity is negligibly small; 6) during the insignificant temperature change of the ampul the pressure remains constant, so that the measured specific heat is isobaric.

From the thermal balance equation of the measurement cell we have

$$\text{const} = W = V\rho c_p \frac{\partial t}{\partial \tau} - \lambda F_1 \left(\frac{\partial t}{\partial r}\right)_{R_1}. \quad (1)$$

During the measurement the ampul temperature changes along curve 2 of Fig. 2 from $\theta'_{\min}$ to $\theta''_{\max}$, intersecting the line t_a (horizontal) at the point b. Here the direction of the thermal flux q changes. Thus, at point b q = 0 and we have adiabatic heating of the liquid, so that $(\partial t/\partial r)_{R_1} = 0$ and

$$W = Vc'_p b^0, \quad (2)$$

where $b^0 = (\partial t/\partial \tau)_b$ is the heating rate at point b.

With consideration of the ballast provided by the ampul and other elements and heat loss to the heater and thermocouple leads, as well as along the tube, Eq. (2) transforms to

$$W - W' = Vc'_p b^0 + C_b b^0 \quad (3)$$

whence

$$c'_p = \frac{1}{V}\left(\frac{W - W'}{b_0} - C_b\right). \quad (4)$$

The annular liquid layer surrounding the ampul also participates in the heating process. Therefore, according to [7], to the volume V we must introduce the corrrection:

$$c'_p = \frac{\dfrac{W - W'}{b^0} - C_b}{V\left(1 + \dfrac{2}{3}\dfrac{\delta}{R_1}\right)}. \quad (5)$$

Equation (5) is valid for the case $\ell \gg R_1$ (where ℓ is the ampul length). If ℓ is relatively small, then with consideration of the heat capacity of the end layers Eq. (5) takes on the form

$$c'_p = \frac{\dfrac{W - W'}{b^0} - C_b}{V\left(1 + \dfrac{2\delta}{3R_1} + \dfrac{2\delta'}{3l}\right)}. \quad (6)$$

In determining b_0 we may use the expression $b_0 = \Delta t/\Delta\tau$ in the vicinity of the point b for a brief time interval $\Delta\tau$. Here Δt must be centered about the point b.

We will derive the computation equation for thermal conductivity with the following assumptions: 1) all assumptions made in deriving the specific heat equation remain in force; 2) the cylindrical (inorganic) surfaces have no eccentricity; 3) heat from the core is transferred through the studied layer, only by conduction; 4) the liquids filling the ampul and annular gap are different, with the volume heat capacity of the first significantly exceeding that of the second $c_1' > c'$.

We now have the thermal balance equation for the core, Eq. (1), where W is the electrical power, $V\rho c_p\, \partial t/\partial\tau = Vc'_p\, \partial t/\partial\tau$ is the thermal power absorbed by the core, $\lambda F_1(\partial t/\partial r)_{R_1}$ is the thermal flux through the annular layer under study.

We will first define $\partial t/\partial\tau$ and $(\partial t/\partial r)_{R_1}$. It follows from curve 2 of Fig. 2 that after regularization of the system (double cylinder) both the core temperature and the temperature of the annular layer change strictly by the same law, determined essentially by the system heating rate m.

Then for the core

$$\theta_c = \theta^c_{\max}[1 - \exp(-m\tau)], \quad (7)$$

where $\theta_c = t_c - t_{\min}$ is the change in core temperature from the initial heating temperature $t_{\min}$; $\theta^c_{\max}$ is the maximum change in core temperature (at the moment the steady-state temperature regime sets in). It is assumed here that the core temperature field is uniform.

The temperature of the liquid layer under study is defined by the equation

$$\theta_{\ell} = B_1 - B_2 [J_0(\mu r) + DY_0(\mu r)] \exp(-m\tau), \tag{8}$$

where $\mu\sqrt{m/a}$; B_1, B_2, D are constants determined by the boundary conditions and physical properties of the liquid. At $\tau = \infty$ (steady-state regime)

$$\theta^{\ell}_{\max} = B_1 = \theta^{c}_{\max} - \frac{\theta^{c}_{\max} - \theta'_{\min}}{\ln k} \ln \frac{r}{R_1},$$

where $k = R_2/R_1$ is the ratio of the radii of the annular layers. At $r = R_2$ $\theta_{\ell} = \theta'_{\min}$; at $r = R_1$ $\theta_{\ell} = \theta_{c}$.

From the first boundary condition

$$B_1(R_2) - B_2 [J_0(\mu R_2) + DY_0(\mu R_2)] \exp(-m\tau) = \theta'_{min},$$

since $B_1(R_2) = \theta'_{\min}$,

$$J_0(\mu R_2) + DY_0(\mu R_2) = 0,$$

or

$$D = -\frac{J_0(\mu R_2)}{Y_0(\mu R_2)}.$$

From the second condition

$$B_1(R_1) - B_2 [J_0(\mu R_1) + DY_0(\mu R_1)] \exp(-m\tau) = \theta^{\text{я}}_{\max} [1 - \exp(-m\tau)].$$

Since $B_1(R_1) = \theta^{c}_{\max}$,

$$B_2 [J_0(\mu R_1) + DY_0(\mu R_1)] = \theta^{c}_{\max},$$

$$B_2 = \frac{\theta^{c}_{\max}}{J_0(\mu R_1) + DY_0(\mu R_1)}.$$

Then from Eq. (8)

$$\theta_{\ell} = \theta^{c}_{\max} - \frac{\theta^{c}_{\max} - \theta'_{\min}}{\ln k} \ln \frac{r}{R_1} - \frac{\theta^{c}_{\max} [J_0(\mu r) + DY_0(\mu r)] \exp(-m\tau)}{J_0(\mu R_1) + DY_0(\mu R_1)}. \tag{9}$$

From Eq. (7) we find

$$\frac{\partial \theta_{c}}{\partial \tau} = \frac{\partial t}{\partial \tau} = \theta^{c}_{\max} m \exp(-m\tau), \tag{10}$$

and from Eq. (9)

$$\left(\frac{\partial \theta_{\ell}}{\partial r}\right)_{R_1} = \left(\frac{\partial t}{\partial r}\right)_{R_1} = -\frac{\theta^{c}_{\max} - \theta'_{\min}}{R_1 \ln k} + \frac{\theta^{c}_{\max} \mu [J_1(\mu R_1) + DY_1(\mu R_1)]}{J_0(\mu R_1) + DY_0(\mu R_1)} \exp(-m\tau). \tag{11}$$

After simplification Eq. (1) takes on the form

$$\omega = \rho_1 c_1 \frac{\partial \theta_{c}}{\partial \tau} - \frac{2\lambda}{R_1} \left(\frac{\partial \theta_{\ell}}{\partial r}\right)_{R_1}, \tag{12}$$

where $\omega = \text{const} = W/(\tau R_1^2 \ell)$ is the specific thermal power; ρ_1, c_1 are the density and specific heat of the core material.

With consideration of Eqs. (10), (11), we obtain from Eq. (12)

$$\omega = \rho_1 c_1 \theta^{c}_{\max} m \exp(-m\tau) + \frac{2\lambda}{R_1} \frac{\theta^{c}_{\max} - \theta'_{\min}}{R_1 \ln k} - \frac{2\lambda \theta^{c}_{\max} \mu [J_1(\mu R_1) + DY_1(\mu R_1)]}{R_1 [J_0(\mu R_1) + DY_0(\mu R_1)]} \exp(-m\tau). \tag{13}$$

At $\tau = \infty$ from Eq. (13) we have

$$\omega = \frac{2\lambda}{R_1} \frac{\theta^{c}_{\max} - \theta'_{\min}}{R_1 \ln k}. \tag{14}$$

Therefore, it follows from Eq. (13) that

$$\rho_1 c_1 \theta^{c}_{\max} m = \frac{2\lambda \theta^{c}_{\max} \mu [J_1(\mu R_1) + DY_1(\mu R_1)]}{R_1 [J_0(\mu R_1) + DY_0(\mu R_1)]},$$

since ω = const. After substitution of the value of D in this expression we define the thermal conductivity coefficient of the layer under study:

$$\lambda = \frac{\rho_1 c_1 R_1 m}{2} \frac{J_0(\mu R_1) Y_0(\mu R_2) - J_0(\mu R_2) Y_0(\mu R_1)}{\mu [J_1(\mu R_1) Y_0(\mu R_2) - J_0(\mu R_2) Y_1(\mu R_1)]}. \tag{15}$$

Using the properties of expansion in Bessel functions and applying the method of successive approximations [7], Eq. (15) can be transformed to the form

$$\lambda = \frac{\rho_1 c_1 m \delta R_1 \gamma}{2} \left(1 + \frac{2\delta}{3R_1} \frac{c\rho}{c_1 \rho_1} \right), \tag{16}$$

where $\delta = R_2 - R_1$; $\gamma = R_1/(R_2 - R_1) \ln k$. The expression in brackets is the correction for heat capacity of the layer under study, which for liquids reaches up to 2% (if δ = 0.05 cm, R_1 = 1.0 cm).

If the liquid in the core and annular layer are one and the same, then from Eq. (16) we obtain

$$\lambda = \frac{\rho c m \delta R_1 \gamma}{2} \left(1 + \frac{2\delta}{3R_1} \right). \tag{17}$$

With consideration of core heat exchange through the end surfaces

$$\lambda = \frac{\rho c m \delta R_1 \gamma}{2} \left(1 + \frac{2\delta}{3R_1} + \frac{2\delta'}{3l} \right). \tag{18}$$

The value of the volume heat capacity $\rho c = c'$ can be defined from Eq. (6), while the heating rate is determined experimentally.

With the aid of Eq. (18) we can write a computation equation for calculation of the thermal diffusivity coefficient

$$a = \frac{m \delta R_1 \gamma}{2} \left(1 + \frac{2\delta}{3R_1} + \frac{2\delta'}{3l} \right). \tag{19}$$

Equation (15) was obtained for the case of an infinite cylinder, where $\ell \gg R_1$. For a finite cylinder we have [8]

$$\lambda = \frac{\rho c R_1 m}{2} \frac{J_0(\mu R_1) Y_0(\mu R_2) - J_0(\mu R_2) Y_0(\mu R_1)}{\sqrt{\mu - \frac{\pi^2}{l^2}} \, [J_1(\mu R_1) Y_0(\mu R_2) - J_0(\mu R_2) Y_1(\mu R_1)]}. \tag{20}$$

Calculations show that at ℓ = 10 cm, R_1 = 1 cm, δ = 0.05 cm the error of Eq. (15) with respect to Eq. (20) comprises only 0.13%, i.e., Eq. (15) gives a somewhat reduced value:

$$\frac{1}{\sqrt{1 - \frac{\pi^2}{l^2 \mu^2}}} = \frac{1}{\sqrt{1 - \frac{\pi^2}{l^2} \frac{R_1^2 \ln k}{2}}} \approx 1.0013.$$

Thus, it can be stated that Eqs. (18), (19) are sufficiently accurate for calculation of λ and a. Finally, these equations take on the form

$$\lambda = \frac{\varphi \rho c \delta m R_1 \gamma}{2} \left(1 + \frac{2\delta}{3R_1} + \frac{2\delta'}{3l} \right) - B, \tag{21}$$

$$a = \frac{\varphi \delta m R_1 \gamma}{2} \left(1 + \frac{2\delta}{3R_1} + \frac{2\delta'}{3l} \right) - B, \tag{22}$$

where φ is a coefficient which considers the specific heat of the core shell and other metallic elements, $\varphi = (V\rho c + C_b)/V_c \rho c$; B is a correction for heat loss along wires, tube, and the centering pins.

In addition, it is necessary to consider the change in geometric dimensions of the cell as a function of temperature and pressure.

Analysis of Eqs. (6), (21), (22) shows that the uncertainty in determination of isobaric specific heat, and the thermal conductivity and diffusivity coefficients of liquids will depend on the uncertainty in determination of the geometric dimensions of the measurement cell, the ballast heat capacity, the galvanometer needle displacement time, and errors involved in calculating the corrections for heat loss along the high pressure tube, positioning of the differential thermocouple junctions, etc.

In our opinion, the most important of the corrections to the fundamental equations are the corrections for heat loss along the steel tube 6 (see Fig. 1) and for location of the thermocouple junctions.

Methods and equations for calculating these corrections are complicated and will be considered in a separate study.

For radial device construction and proper consideration of all possible corrections the uncertainty in determining isobaric specific heat should not exceed 1.5-2%, that in the thermal conductivity should be no more than 2-2.5%, and that in thermal diffusivity, 1-1.5%.

For practical use of Eqs. (21), (22) it is necessary to determine the value of m experimentally. Several methods of determining m are possible.

Method One. From Eqs. (10) and (7) at point b we have

$$b^0 = m\theta^{c}_{max}\exp(-m\tau_b), \tag{23}$$

$$\theta'_{min} = \theta^{c}_{max} - \theta^{c}_{max}\exp(-m\tau_b), \tag{24}$$

but $\theta^{c}_{max} = \theta'_{min} + \theta''_{max}$, then from the last equation it follows that $\theta''_{max} = \theta^{c}_{max}\exp(-m\tau_b)$.

Substituting the last expression in Eq. (23), we obtain

$$m = \frac{b^0}{\theta''_{max}}. \tag{25}$$

This expression is convenient for determining m, if the quantity θ^{c}_{max} is known. The value of b^0 has already been determined in calculating c' with Eq. (6), while $\theta''_{max} = t_{max} - t_a$ can be measured with a differential thermocouple in the steady-state regime. However, precise determination of θ^{c}_{max} is difficult and requires a definite time for onset of the steady-state regime.

Method Two. For the point b we have

$$b^0 = m\theta''_{max},$$

for point c,

$$b_{\ell} = m(\theta''_{max} - \theta''_{\ell});$$

and after subtraction of the second equation from the first we have

$$b^0 - b_c = m\theta''_c$$

and

$$m = \frac{b^0 - b_c}{\theta''_c}, \tag{26}$$

where $b_c = (\partial\theta/\partial\tau)$ is the heating rate at point c. Here definition of θ''_c does not require a great deal of time, but does not have high accuracy.

Method Three. If we measure temperature, for example, from t_{max}, then m can be determined very easily. In addition, the accuracy of heating rate determination will be quite high due to its independence from the absolute value of θ. Here θ can be replaced by values of the scale divisions of the galvanometer used to fix the change in temperature difference between the core and autoclave.

Equation (7) can be written in the following manner:

$$\theta^{c}_{max} - \theta_c = \theta^{c}_{max}\exp(-m\tau). \tag{27}$$

Denoting $\theta^{c}_{max} - \theta_c = v_c$ (at $\theta_c = 0$ $\theta^{c}_{max} = v^{c}_{max}$) we obtain $v_c = \theta^{c}_{max}\exp(-m\tau)$. Then for two neighboring points b' and b", in the interval between which the heating velocity b^0 is measured, we obtain

$$v'_c = \theta^{c}_{max}\exp(-m\tau'), \quad v''_c = \theta^{c}_{max}\exp(-m\tau''),$$

or

$$\ln v'_c = \ln\theta^{c}_{max} - m\tau', \quad \ln v''_c = \ln\theta^{c}_{max} - m\tau'',$$

and finally,

$$m(\tau''-\tau')=\ln v'_c-\ln v''_c$$

$$m=\frac{\ln v'_c-\ln v''_c}{\Delta\tau}, \qquad (28)$$

where $\Delta\tau = \tau'' - \tau'$ is the time over which the temperature difference changes in the interval b' − b". It is convenient to use the galvanometer scale divisions, then

$$m=\frac{\ln N_1-\ln N_2}{\Delta\tau}. \qquad (29)$$

Use of Eq. (29) is quite convenient for practical determination of m.

NOTATION

t_a, autoclave temperature; θ, temperature change; V, ρ, c_p, volume, density, and isobaric specific heat of material in ampul; λ, thermal conductivity of heat meter material; F_1, R_1, area and radius of outer ampul surface; c_p', volume isobaric specific heat of material; W', correction required for heat loss along conductive wires and tube; C_b, ballast heat capacity of ampul and other elements; δ, δ', thickness of side and end layers of liquid; a, thermal diffusivity; V_c, core volume.

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THEORY OF BIVACANCY CONTRIBUTION TO THE COEFFICIENT OF SELF-DIFFUSION IN MONATOMIC MOLECULAR CRYSTALS

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On the basis of the statistical theory of a crystal with defects, we calculate the frequency of jumps of an atom for diffusion in the bivacancy mechanism. We obtain an expression for the contributions of different types of bivacancies to the coefficient of self-diffusion. Calculations are carried out for the special case of a Lennard-Jones 6-12 potential.

The vacancy mechanism of diffusion assumes that the coefficient of self-diffusion is determined both by monovacancies as well as complex vacancies. Of the various vacancy clusters, the most important for diffusion are bivacancies, since the concentration of clusters containing a larger number of vacancies rapidly falls off with the number of vacancies.

The known estimates of the contribution of bivacancies to self-diffusion lie in a rather wide range (see for example [1]). The difficulties of such estimates are explained by the fact that they are mostly in the form of independent calculations of two groups of parameters:

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