m_i, mass of newly formed gas molecule; G, second mass gas flow rate; V_z, V_r, V_φ, projections of gas velocity vector; P, gas pressure; k, Boltzmann constant; ρ, density; λ, free path length; T_b, gas temperature at the discharge-chamber inlet; T_R, temperature of inner channel wall; q_c, q_M, loss of heat through cathode and interelectrode insert; d, discharge-chamber diameter; d_a, anode diameter; l, distance between electrodes; c_1, c_2, c_n, constant dimensional coefficients.

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SPECIFIC HEAT OF LIQUID CESIUM AT TEMPERATURES UP TO 2000°K AND PRESSURES UP TO 12 MPa

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UDC 536.63:621.039.534.6

We present and discuss measured values of the specific heat and resistivity of liquid cesium in the temperature range 1200-1950°K at pressures up to 12 MPa.

Considerable progress has been made in the last decade in the study of the thermodynamic and electrical properties of liquid alkali metals and mercury over the whole existence domain of the liquid phase and also in the supercritical region. The results obtained are of interest both from the point of view of understanding the laws of behavior of the thermodynamic parameters of liquid metals over a wide range of states, and also from the point of view of clarifying the nature of the metal–dielectric transition in liquid metals. The aim of the present study is to supplement existing knowledge by data on the caloric properties of the alkali metals (e.g., cesium) in the existence domain of the liquid phase. The experimental results in [1] are discussed here together with new data obtained recently.

The measurements at high temperatures under presssure were made by a method based on the periodic heating of the sample in a high-pressure chamber by an electric current. The measuring cell (sample) was a thin molybdenum tube 150 mm long with a 5.2-mm inside diameter and a 0.15-0.2-mm wall thickness filled with the liquid metal and pressurized by a bellows welded onto the upper end of the cell. The high-pressure chamber was provided with leucosaphire-optical windows which permitted the determination of the reference temperature with an OP-70 optical pyrometer, and the recording of temperature oscillations of the sample surface by a photoelectric described in more detail in [2, 3].

An important feature of the method used is the fact that the sample under study was in a gaseous atmosphere. This necessitated estimating the effect of heat transfer on the specific heat measurements. We also took account of the fact that the sample was a two-layer system consisting of a liquid metal core in a molybdenum shell, and that the components of the system had very different properties. It was necessary to choose and produce experimental conditions to minimize the effect of these factors. To this end we investigated the system of two

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heat-conduction equations for the core and shell with boundary conditions taking account of heat transfer at the shell surface. The solution of this system of equations gave an analytic expression for the amplitude of the temperature oscillations at the sample surface [4]. This solution can be written concisely in the form

$$\theta = \frac{w_1 + w_2}{(c_1 + c_2)\,\omega}\, g\left(\sqrt{\mathrm{Pd}},\ \mathrm{Bi},\ \frac{c_2}{c_1},\ \frac{r_2}{r_1},\ \frac{R_1 - R_2}{R_1}\ \frac{\lambda_1}{\lambda_2}\right).$$

The factor g is a complicated dimensionless function of five dimensionless quantitites including the Predvoditelev number $\mathrm{Pd} = \omega^2/a_1 R_1^2$ (a is the thermal diffusivity) and the Biot number $\mathrm{Bi} = \alpha R_1/\lambda_1$. For values of the variables corresponding to the actual experimental conditions the factor g is close to unity. At low frequencies heat transfer has a decisive effect on the behavior of the correction factor and $g < 1$; at high frequencies the effect related to the damping of the temperature wave propagating from the wall to the axis of the sample predominates, and $g > 1$. Thus, there is a frequency range where these effects compensate one another. Taking account of the properties of the liquid metal sample and the cell and the geometry, it was found that the optimum frequency range is 1-3 Hz. Even under the most unfavorable experimental conditions when, for example, the temperature is 1950°K and the pressure is 119 bar, $g = 0.992$.

In addition to the effect of heat transfer and damping of the temperature wave, it is important to determine the effect of convection of the liquid metal within the cell on the measurement of the specific heat. Therefore, in the last series of measurements the experiments were performed with a cell provided with molybdenum foil baffles 0.05 mm thick. Two baffles were mounted above the working portion and one below. These should substantially decrease convection of the liquid metal in the region of high temperature gradients. A comparison of the results obtained with and without the baffles showed that they had little effect, i.e., their effect did not exceed the spread of data attributable to other factors.

The random error of a single measurement of the total heat capacity of the sample, including the heat capacity of the cell wall, was ∿5% on the average. The random error of the determination of the heat capacity of the liquid cesium itself was ∿10% because of the unfavorable ratio of the heat capacity of the liquid metal to that of the cell wall. The systematic error of the measurement of the specific heat of cesium was 11-14%. The largest contributions to this error were from the measurement of the average temperature, the specific heat of the cell wall material, and its thickness. The error in the determination of the average temperature makes two contributions to the error of the determination of the heat capacity. Depending on the experimental conditions, these contributions are either subtracted or added, and this determines the limits of systematic error mentioned above. It should be emphasized that the error is not overly large, if the unfavorable experimental conditions are taken into account. It should be added that the use of ten different cells in the experiments to a large extent randomizes the contribution of the error in the determination of the dimensions of these cells to the systematic error, and reduces it by ∿2% to 9-12%.

The arrangement permitted the direct measurement of the volumetric heat capacity $c_p d$ (c_p is the specific heat and d is the density). The measurements were performed at temperatures from 1200 to 1950°K and pressures from 4.5 to 13.6 MPa.

Measurements of the resistance showed that cesium retains its metallic conductivity character up to 1950°K, since over the whole temperature range studied its resistivity remained below the limit of metallic conductivity for the alkali metals, which, according to estimates in [5], is 3000-5000 μΩ·cm. This confirms Hensel's view that the metal–dielectric transition in alkali metals is near the critical point.

Another result obtained from the measurement of the resistivity of liquid cesium at various temperatures and pressures should be noted. It is known that the disordered set of curves of the temperature dependence of the resistivity of metals becomes orderly if the specific volume instead of the temperature is used as the independent variable [6-8]. The data presented below show that the dependence of the resistivity on volume also gives the dependence on temperature and pressure, which confirms the view that volume plays a special role as a geometric factor in the physics of a liquid. This factor is plotted in Fig. 1 (the density was determined from p–V–T data in [9]). The unsmoothed experimental points plotted on the figure were obtained at widely different temperatures and pressures. In spite of the spread of the points, a rather simple nearly linear dependence of ρ on the density can be traced.

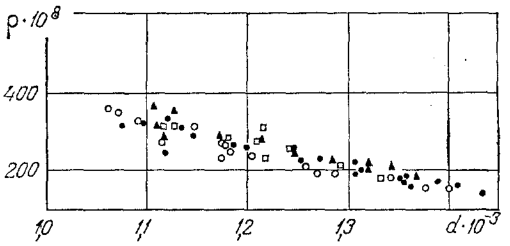

Fig. 1

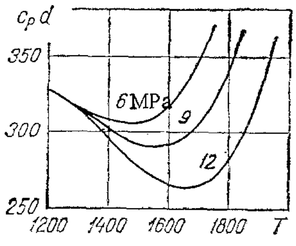

Fig. 2

Fig. 1. Resistivity ρ (Ωm) of liquid cesium as a function of density d (kg/m^3). Experimental points were obtained at various pressures and temperatures.

Fig. 2. Smoothed temperature dependences of volumetric heat capacity $c_p d$ (kJ/m^3·K) of liquid cesium.

TABLE 1. Polynomial Coefficients A_{ij}

j	i			
	0	1	2	3
0	—1111,861	0,389580·10	—0,342469·10^{-2}	0,980765·10^{-6}
1	—0,785359·10^2	0,132217	—0,554079·10^{-4}	—

The volumetric heat capacity of liquid cesium at constant pressure was measured over the same range of temperatures and pressures used in measuring the resistivity. More than 100 experimental points were obtained. The values of $c_p d$ were smoothed by the least-squares method, using the double polynomial

$$c_p(p,\ T)\,d = \sum_{i=0}^{n}\sum_{j=0}^{m} A_{ij}T^i p^j, \tag{1}$$

where T is the absolute temperature (°K); p, pressure (MPa); d, density (kg/m^3); and c_p, specific heat (kJ/kg·K).

Table 1 lists the values of the coefficients A_{ij} of the polynomial (1). The mean-square deviation of the experimental points from the smoothed values is ~10%. The main contribution to the random error comes from the fluctuations of the emittance of the sample due to the convection of argon.

Figure 2 shows the smoothed temperature dependences of the volumetric heat capacity $c_p d$ for pressures of 6, 9, and 12 MPa. In the temperature range investigated the effect of pressure on heat capacity increases with temperature. This permits a comparison of data on the caloric and thermal equations of state by using the well-known thermodynamic relation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p,$$

where V is the specific volume. A comparison of the values of $(\partial c_p/\partial p)_T$ obtained from our data on $c_p d$ and data on d from [9] with values of the derivative $(-1)T(\partial^2V/\partial T^2)_p$ found from the p—V—T data of Korshunov et al. [9] showed that in spite of the large spread of values of $(-1)T(\partial^2V/\partial T^2)_p$ resulting from the loss of accuracy in the double differentiation, there is qualitative agreement of the values obtained from caloric and thermal data.

The values of the volumetric heat capacity determined from Eq. (1) and tables can be converted into values of the molar heat capacity by using data on the equation of state of liquid cesium [9]. The isobars of the molar heat capacity corresponding to pressures of 6, 9, and 12 MPa are shown in Fig. 3. Using Eq. (1) and the p—V—T data, the values of the molar heat capacity c_p on the saturation line (curve 1 of Fig. 3) were found also. Data on the vapor pressure [10] and density [10, 11] of liquid cesium on the saturation line were used to refine the parameters. Curve 2 of Fig. 3 corresponds to values recommended in [12] for temperatures up to 1500°K. Experimental data obtained at temperatures up to 1300°K were used, and therefore the part of the curve between 1300 and 1500°K is extrapolated. It is clear from Fig. 3 that our data in the low-temperature region are in fair agreement with the recommended values.

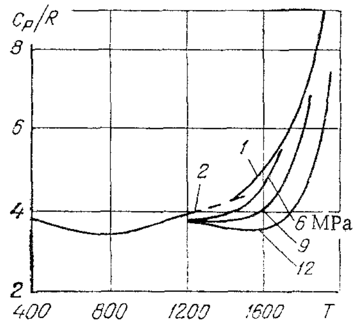

Fig. 3

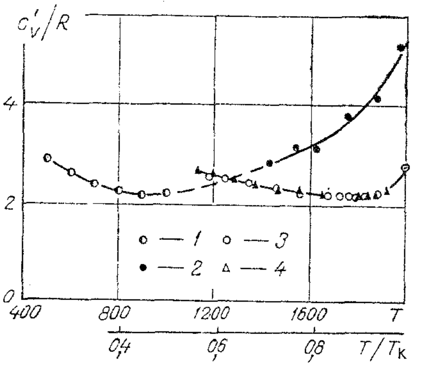

Fig. 4

Fig. 3. Molar heat capacity on the saturation line and isobars of molar heat capacity: curve 1 and isobars 6, 9, and 12 MPa — or data; 2) values recommended in [12].

Fig. 4. Specific heat c_V of cesium at constant volume on the saturation line: 1) according to data in [14]; 2) our results; 3, 4) c_V of argon and krypton [15, 16].

To determine the specific heat at constant volume c_V, it is necessary to use results for the isothermal compressibility $\beta_T = (-1)(1/V)(\partial V/\partial p)_T$ and the coefficient of the thermal expansion $\alpha p = (1/V)(\partial V/\partial T)_P$ in addition to data on c_P. There are not data on the compressibility of liquid cesium at temperatures above 1300°K, but by using the p–V–T data in [9], values of the compressibility and also the coefficient of thermal expansion can be found. Using the approximate values of α_P and β_T obtained in this way, the specific heat of cesium at constant volume can be estimated from the formula

$$c_V = c_P - TV\alpha_p^2/\beta_T\,.$$

If the electron specific heat is subtracted from the specific heat of a liquid metal at constant volume, the difference will represent the specific heat of the ionic subsystem at constant volume, and this should be compared with the specific heat of monatomic dielectric liquids (e.g., liquefied inert gases) to determine the similarities and differences in the behavior of metallic and nonmetallic monatomic liquids. The electron specific heat was estimated from the formula $c_{el} = \gamma T$. Since there are no data on c_{el} for liquid cesium, we used the value of γ obtained for the solid phase in [13]: $\gamma = (3201 \pm 1047) \times 10^{-6}$ kJ/K•kmole. Figure 4 shows our values of the specific heat $c_V' = c_V - c_{el}$ of liquid cesium in the range 1400-1950°C. Estimates of c_V for liquid cesium in the range 400-1100°K can be found in the literature. In [14] values of c_V were found by using known data on c_p and the coefficient of thermal expansion on the saturation line, and also by using values of the adiabatic compressibility of liquid cesium obtained by the authors from a measurement of the speed of ultrasound. Figure 4 shows these values after the subtraction of the electron contribution to the specific heat (curve 1).

A combination of our results with data of [14] in the low temperature region shows a minimum of c_V as a function of T in the range $T/T_{crit} = 0.5$-0.6.* At the same time the minimum of the specific heat of argon and krypton at constant volume on the saturation line occurs near $T/T_{crit} = 0.9$ (curve on Fig. 4 drawn through points 3 and 4 [15, 16]). The increase in the specific heat of these substances as the critical point is approached is related to critical fluctuations. For cesium there is no basis for assuming that the increase of c_V at $T/T_{crit} = 0.6$ can be the result of critical fluctuations. This behavior of the specific heat of cesium at constant volume may be related to the nature of the interatomic interaction in liquid metals. It is known that in liquid metals the depth of the potential well of the effective pair interionic potential increases by a considerable factor for a decrease in density from values corresponding to the triple point to values near the critical density [17, 18]. According to [19], an approximate expression for c_V which takes account of pair correlations only has the form

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*Theoretical calculations confirming the existence of a minimum of $c_V(T)$ for the alkali metals have just been published. (A. M. Bratkovskii, "The theory of structural and thermodynamic properties of the liquid phase and the melting of the alkali metals," Author's Abstract of Candidate's Dissertation, Moscow (1982), p. 20.).

$$c_V \simeq \frac{3}{2}R + \frac{2\pi N}{K_B V T^2}\int_0^\infty \Phi^2(r)\, g(r)\, r^2 dr.$$

Since the integrand contains $\Phi^2(r)$, there is a basis for assuming that the strong dependence of the depth of the potential well on the density, which is peculiar to metals, may be due to the difference in the nature of the temperature (density) dependence of the specific heat of metallic and nonmetallic monatomic liquids at constant volume.

NOTATION

θ, amplitude of temperature pulsations; ω, modulation frequency; w_1, power (amplitude of variable power component) liberated by cesium; w_2, power liberated by molybdenum tube; r_1, resistance of cesium; r_2, resistance of molybdenum tube; c_1, total heat capacity of part of cesium measured; c_2, total heat capacity of part of molybdenum tube measured; R_1 and R_2, inside and outside radii of molbydenum tube, respectively; λ_1, thermal conductivity of cesium; λ_2, thermal conductivity of molbydenum; α, heat-transfer coefficient; c_V, specific heat at constant volume; α_P, coefficient of thermal expansion; β_T, isothermal compressibility; c_{el}, electron specific heat of cesium; ρ, resistivity of cesium; $\Phi(r)$, effective pair potential; $g(r)$, radial distribution function.

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STUDY OF MODEL INTERACTION POTENTIALS OF MULTIATOMIC MOLECULES IN LIQUIDS BY PERTURBATION THEORY II. MODEL POTENTIALS FOR CCl₄

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The results of calculation of thermodynamic properties of liquids with intermolecular potentials modeling CCl_4 are presented.

The possibility of using perturbation theory in the Verlet—Weis formulation for the study of effective pair interaction potentials of molecules in liquids has been considered in [1]. Below we use this method to study various model potentials whose parameters correspond to the characteristics of the CCl_4 molecule. The term model, as also used earlier in [2-4], is understood to comprise potentials where all parameters are determined from the molecular structure and the physical interaction model under consideration, and do not contain adjustable parameters. Methods of determining model potential parameters from the molecular structure have been discussed in [2]. The molecule CCl_4 is particularly suitable for this type of analysis since it has been studied in detail [5, 6] and hence there is abundant data for comparison; also the symmetry of the molecule eliminates certain ambiguities in what is meant by "peripheral atoms" and "center of the molecule" which occur in the determination of model potential parameters in [2, 4, 7]. Also the CCl_4 molecule significantly differs from a point force center as can be seen by the value determining the similtude number A [8, 9] which is equal to 2.06 for this material (recall that $A = 4$ for an inert gas).

In the present paper, we study potentials selected from a number of forms considered earlier [2, 4] by different methods [7]. The potentials considered here have the form

$$\frac{u}{\varepsilon} = f_{12}\left(\frac{r}{\sigma},\ \alpha\right) - 2f_6\left(\frac{r}{\sigma},\ \alpha\right), \tag{1}$$

where $f_{12}(t, 0) = t^{-12}$; $f_6(t, 0) = t^{-6}$. The parameters ε, σ, and α corresponding to the CCl_4 molecule are given by

$$\sigma = \sigma_{Cl} = 3.55\,\mathring{A}\ [7], \tag{2}$$

$$d_{C-Cl} = 1.766\mathring{A},$$

$$\alpha = d/\sigma = 2d_{C-Cl}/\sigma = 1{,}00, \tag{3}$$

$$\varepsilon = c/\sigma^6,$$

$$c = (4\sqrt{c_{Cl}} + \sqrt{c_C})^2,$$

$$\sqrt{c_{Cl}} = 2.36;\ \sqrt{c_C} = 1.14\ [7], \tag{4}$$

and hence

$$\varepsilon/k = 6726\,\mathrm{K}.$$

The following functions were taken for f_n:

$$f_n^{ss} = \frac{1}{(n-2)(n-3)\alpha^2 R} P^{(n-3)}(R,\ \alpha) \tag{5}$$

(spherical shell potential)

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