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GENERAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF ALKALINE EARTH METALS

É. É. Shpil'rain, D. N. Kagan,
V. A. Fomin, V. V. Kachalov,
S. N. Ul'yanov, and G. F. Sokol

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Several experimental devices are used to measure the density, surface tension, viscosity, and heat capacity of barium, calcium, and cesium from their melting points to 1800°K. Measurement methods are described and results presented.

Introduction. Liquid alkaline earth metals are of significant interest as working substances in heat exchangers at significantly higher temperatures than those of alkali metals. Among many types of power equipment which use alkaline earth metals, we must note specially high-temperature thermal tubes. The present study was undertaken because development of new technology requires data on the thermophysical characteristics of these materials, although appropriate information is still absent from the literature.

A complex of experimental equipment was developed that permitted measurement of density, surface tension, viscosity and heat capacity of liquid alkaline earth metals up to temperatures of about 1800°K. The studies were performed with specimens at least 99% pure, with all specimen preparation and ampul loading performed in an atmosphere of purified dry argon. Analysis of the metals after the experiments revealed the absence of any significant solubility of the construction materials over the time of the experiments.

Experiments. 1. Density and Surface Tension. The density of the specimens studied was measured by the method of maximum pressure in a gas bubble. The density values were obtained by processing the maximum bubble formation pressure as a function of capillary immersion depth in the melt by the least-squares method. The relative immersion depth was calculated from the displacement of the upper end of the capillary tube, maintained at room temperature, with consideration of temperature expansions of the crucible and capillary materials and the change in position of the liquid metal meniscus within the crucible due to removal of melt through the capillary.

The surface tension of the materials was measured by the maximum gas bubble pressure method using two capillaries of differing diameters, immersed to different depths in the melt. The surface tension values were calculated with an equation analogous to that of Sugden [1, 2]:

$$D^2 = [(H_1 - H_2) - \Delta h_M] / \left(\frac{1}{X_1} - \frac{1}{X_2} \right), \tag{1}$$

where D^2 is the capillary constant of the material under study, equal to $2\sigma/\rho g$; $X_{1,2}$, "effective" radii of the capillaries, determined by Sugden's tables [1]; Δh_M, a value determined by the distance between the planes of the capillary ends at the experimental temperature and the distance between the meniscus positions in the crucible at the moment of attainment of maximum pressure in bubble formation in the first and second capillaries, respectively.

Thus, the data of a single experiment were used to calculate the density and surface tension of the liquid metals studied.

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TABLE 1. Crucible Characteristics for Viscosity Studies

Metal	$R\cdot10^3$, m	$K\cdot10^5$, kg·m	$M_{work}\cdot10^3$, kg	$M_{cal}\cdot10^3$, kg
Calcium	11,46	87,953	29,270	—
Strontium	6,99	88,632	25,772	5,471
Barium	8,53	84,171	55,093	14,930

The capillaries used in the study of all the metals were made of tantalum and had diameters from 1 to 4 mm. The capillary diameters were measured in two mutually perpendicular planes by an IZS-2 comparator to an accuracy of 0.001 mm. The wall thickness at the capillary end did not exceed 0.01 mm. The bell-shaped crucible had a diameter of about 40 mm at its wide part and was made of tantalum for the barium study, and of molybdenum for the calcium and strontium studies. Use of this crucible shape permitted a reduction in volume of metal under study while retaining the possibility of deep immersion of the capillaries, necessary for the density calculation and to minimize the correction for meniscus displacement due to capillary immersion. Pulse tubes and shield screen were made of molybdenum. The drive mechanism used ensured strictly vertical motion of the capillaries. Before filling with the metal, the working region was degasified in a vacuum of $\sim10^{-5}$ mm Hg at temperatures 200-300° higher than the maximum experimental temperatures.

The experiments were performed in a vertical vacuum furnace. All possible vibration sources were decoupled from the furnace body by flexible mountings. To decrease the effect of the heater's electromagnetic field on the liquid metal and stabilize the temperature field over height, the heater was constructed in the form of bifilar wound vertical tungsten bars 3 mm in diameter. The pressure of the inert gas producing the gas bubble was measured by a U-shaped manometer filled with PFMS-2/5 1 siloxane oil, which has a low viscosity and vapor pressure at room temperature. The manometric liquid was temperature-stabilized within 0.01° using a U-10 thermostat. The position of the manometer liquid meniscus was recorded by a KM-8 cathetometer to an accuracy of 0.01 mm. The displacement of the cold ends of the capillaries was measured by an IZV-21 optimeter to an accuracy of 0.001 mm. The liquid metal temperature was measured by three PR-6/30 thermocouples, located in a massive molybdenum block.

The bubbles were formed with type VCh helium, which was additionally purified in a titanium column at a temperature of 800°C, in a calcium column at 300-350°C, and with activated carbon at liquid nitrogen temperature. The time required for formation of one bubble was about 10 sec. In each temperature regime the maximum bubble formation pressure was recorded at 10-20 immersion levels. The greatest immersion depth was about 20 mm. The maximum pressure at each level was the average of 5-10 manometer indications for different bubbles. The divergence between the manometer indications at each depth during immersion and extraction of the capillaries was within the limits of the scattering of the maximum pressure values.

2. Viscosity was determined by the absolute variant of the torsion-oscillatory method with a cylindrical crucible and the free surface of the melt within the crucible. Shvidkovskii [3] has presented the theory of the method [3].

The formula used for the calculation is the following:

TABLE 2. Characteristics of Density and Surface Tension Data

Metal	Temp. range T, °K	$a\cdot10^{-3}$, kg/m³	b, °K⁻¹	$c\cdot10^3$, N/m
Ca	1162—1840	1,5501	0,0001760	490,68
Sr	1097—1683	2,5267	0,0002101	367,76
Ba	1039—1852	3,67528	0,0003239	335,70

Metal	d, °K⁻¹	$S_\rho\cdot10^{-3}$, kg/m³	$S_\sigma\cdot10^3$, N/m	Δ_ρ, %	Δ_σ, %
Ca	0,11245	0,0040	2,67	1,1	1,7
Sr	0,07521	0,0070	2,58	0,72	1,9
Ba	0,06903	0,0064	1,48	0,5	2

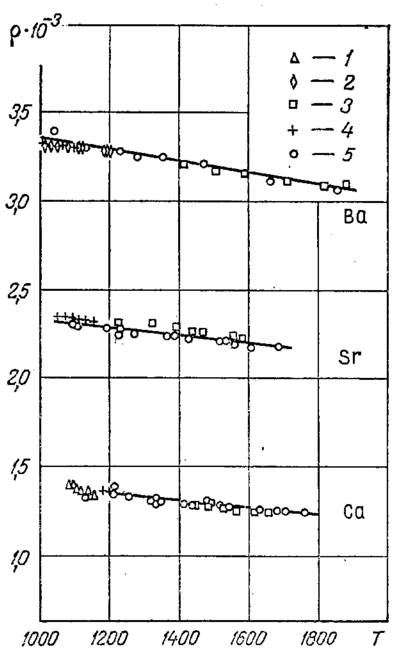

Fig. 1

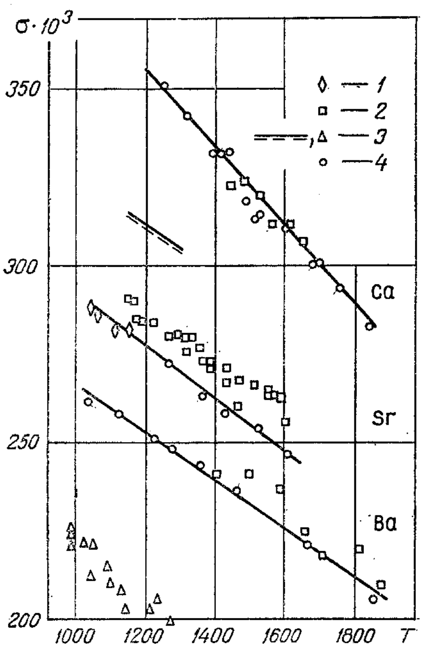

Fig. 2

Fig. 1. Density versus temperature: 1) experiment [5]; 2) [4]; 3) [6]; 4) [7]; 5) High-Temperature Institute data. ρ, kg/m³; T, °K.

Fig. 2. Surface tension versus temperature: 1) data of [8]; 2) [6]; 3) [9]; 4) High-Temperature Institute data. σ, N/m.

$$\nu = \frac{1}{\pi}\left(\frac{K}{MR}\right)^2\left(\delta - \frac{t}{t_0}\delta_0\right)\Big/ t\psi^2, \tag{2}$$

where

$$\psi = 1 - \frac{3}{2}Z - \frac{3}{8}Z^2 - \alpha + \frac{2nR}{2h}(\beta - \gamma Z),$$
$$\alpha = 3/\sqrt{2y};\quad y = R^2 2\pi/\tau\nu_*,\quad Z = \delta/2\pi. \tag{3}$$

The calculation is performed by the iteration method.

This technique was used only for the study of calcium. It was assumed that $n = 2$ with consideration of the form and state of the open metal surface, methodical experiments on other liquids, and previous studies with alkali metals. In the study of barium and strontium, as a result of measurements with two fillings of one and the same crucible, the value $n = 0$ was chosen with corresponding changes in M and ΔM in Eq. (2). The calibration parameters of the oscillations in this case were the oscillation parameters of the less filled

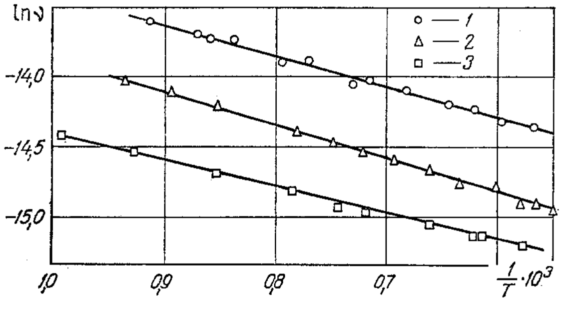

Fig. 3. Viscosity versus temperature: 1) calcium; 2) strontium; 3) barium. ν, m²/sec.

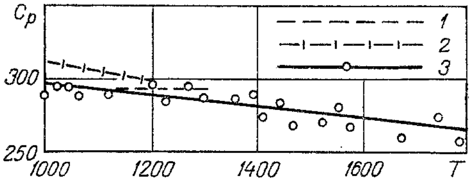

Fig. 4. Heat capacity versus temperature: 1) data of [10]; 2) [11]; 3) High-Temperature Institute data. C_p, J/kg·deg.

system. Thus, the oscillations of a liquid column of mass ΔM in the working experiment were considered free of the effect of the confining faces, and the contribution to the oscillation parameters of the end (both bottom and meniscus) portions of the liquid were considered in the calibration experiment.

The main component of the viscosimeter — the suspension system — was contained in a vacuum resistance furnace the same as that used in the density and surface tension studies. The mechanical oscillations had an amplitude of about 5° and were recorded by a reflected light beam. The crucible was of welded molybdenum (tantalum was used for the barium studies).

Table 1 presents the geometric parameters of the crucibles used at room temperature and the masses of metal used to fill them.

3. Heat capacity was determined by a pulse differential technique, based on comparison of the rates of temperature change of the specimen under study and a reference with a step-like change in temperature of the surrounding medium. With the technique used the size of this temperature pulse was small in comparison to the steady-state temperature level. With radiant heat exchange under vacuum furnace conditions, the rate of change of temperature of the specimen suspended within a tubular heater, the temperature of which changes abruptly, is dependent solely on the total heat capacity of the specimen and the value of the thermal flux q upon its surface

$$CM\,(dT/d\tau) = q. \tag{4}$$

For each concrete temperature value the magnitude of q is determined solely by the specimen surface parameters, and does not depend on the specimen's thermophysical properties. Therefore q may be determined by using a specimen of known heat capacity under the same conditions. Then for identical specimen surface temperatures and heater temperatures the thermal fluxes will be equal, provided, of course, that the form, size, and surface radiant characteristics of both specimens are the same. It is sufficient to obtain thermograms of the transition processes for both specimens and calculate the ratio of the rates of temperature change, so that with a known heat capacity of the reference specimen one can find the desired heat capacity of the material under study:

$$C_{\mathrm{s}} = C_{\mathrm{r}} \frac{M_{\mathrm{r}}}{M_{\mathrm{s}}} \frac{(dT/d\tau)_{\mathrm{r}}}{(dT/d\tau)_{\mathrm{s}}}. \tag{5}$$

In order to equalize the radiation characteristics of the two specimens, the study specimen was placed in a molybdenum container with a thermosensor, and a molybdenum block of the same form and size as the container was used for the reference. Then, with consideration of the effect of the thermosensor and container, we have

$$C_{\mathrm{s}} = C_{\text{э}} \frac{M_{\mathrm{c}}}{M_{\mathrm{s}}} \left[\frac{M_{\mathrm{r}}}{M_{\mathrm{c}}} \frac{(dT/d\tau)_{\mathrm{r}}}{(dT/d\tau)_{\mathrm{s}}} - 1 \right] + C_{\mathrm{t}} \frac{M_{\mathrm{t}}}{M_{\mathrm{s}}} \left[\frac{(dT/d\tau)_{\mathrm{r}}}{(dT/d\tau)_{\mathrm{s}}} - 1 \right]. \tag{6}$$

TABLE 3. Characteristics of Viscosity Data

Metal	Temp. range, °K	$A\cdot 10^3$, Pa·sec	B, °K
Calcium	1096—1763	0,166	2545
Strontium	1072—1824	0,159	2648
Barium	1005—1767	0,215	2098

In processing the results, the spatial temperature distribution within the specimens was considered, allowance being made for the difference between the mean temperature over specimen volume (which appears in Eq. (6)) and the mean temperature over the surface (the identity of which for both specimens is a consequence of fulfillment of Eq. (5)) and the divergence of both these temperatures from the temperature measured in the center of the specimen during the experiment. For calculating the influence of the temperature distribution with respect to the sample, we examined the approximation solution for differential equations of **thermal conductivity in the nonstationary nonlinear case. The corrections obtained for the metal specimens** used did not exceed 0.1%.

The container with specimen was suspended from two molybdenum filaments with ϕ 0.1 mm within a low-inertia tubular niobium vacuum furnace resistance heater. The container diameter was 14 mm; height, 50 mm; wall thickness, 0.3 mm. A capillary was inserted along the axis to the center of the specimen, and a PR 30/6 thermocouple was attached to its bottom. The container was sealed by an electron beam in a vacuum.

Generation of the temperature pulse in the heater and maintenance of a constant temperature level were accomplished with a VRT-3 precision temperature regulator, operating in the proportional integral-differential mode. The value of the temperature step (50-70°K) was chosen experimentally so that the relaxation process in the specimen could be described by the formulas of a type I regular thermal regime, which significantly simplified processing of the measurements. The duration of the transient processes depended significantly on the initial temperature, comprising several tens of sec for the specimen and several sec for the heater on the average. These processes were recorded by a compensation technique of sensor signal measurement, including a Shch 1513 digital voltmeter with an F 595 transcriber and printer. To monitor experimental conditions, a continuous analog readout was carried out with an MS-611-6N recording potentiometer, which recorded the temperatures of both specimen and heater.

Results. The experimental values of density and surface tension of calcium, strontium, and barium are presented in Figs. 1, 2. The least-squares method was applied to this data to obtain equations of the type

$$\rho = a - bT, \tag{7}$$

$$\sigma = c - dT. \tag{8}$$

The values of the coefficients in Eqs. (7), (8), the temperature intervals used, the mean-square deviations of the experimental values from the selected equations S_ρ and S_σ, and the probable error and (at an 0.95 confidence level) Δ_ρ and Δ_σ at maximum experimental temperature are presented in Table 2. Comparison of the present data on density of alkaline-earth metals with results published by other authors [4-7] showed good agreement within the limits of experimental error. For surface tension, the present results agree with data of Lazarev and Pershikov [8] and Bodansky and Schins [6]. The values obtained in [9] appear to be erroneous.

The experimental results on kinematic viscosity of the metals are presented in Fig. 3. The data on dynamic viscosity are approximated well by an exponential expression of the form $\eta = A \cdot \exp(B/T)$. Table 3 presents the values of the constants A and B in this function, together with the temperature ranges studied. At a 95% confidence level the uncertainty of the data is about 5% at the maximum temperatures studied.

The values of liquid barium heat capacity determined experimentally are shown in Fig. 4. They agree with our previous data obtained by enthalpy measurements [10], and with the data of Ditmars and Douglas [11]. The probable uncertainty of the values at the 95% confidence level for high temperatures is 3-5%. The experimental data obtained indicate a decrease in heat capacity of liquid barium with increase in temperature. The data may be approximated by an equation

$$C = 0.3287 - 0.314 \cdot 10^{-4} T.$$

NOTATION

$H_{1,2}$, maximum pressure for bubble formation in first and second capillaries, measured in m of test metal column; g, acceleration of gravity; ρ, density, kg/m^3; σ, surface tension, N/m; T, temperature, °K; ν, kinematic viscosity, m^2/sec; η, dynamic viscosity, Pa·sec; M, mass, kg; K, moment of inertia of crucible, kg·m^2; R, crucible radius, m; δ, δ_0, oscillation damping decrement for working and calibration experiments; t, t_0, crucible oscillation period for working and calibration experiments, sec; 2h, liquid height in crucible, m; n, number of plane surfaces on which liquid is in contact with crucible; β, γ, tabulated functions; C, heat capacity; τ, time; q, thermal flux; A, B, a, b, c, d, coefficients of approximate equations. Subscripts r, c, s, t indicate reference, container, specimen, thermosensor.

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