EXPERIMENTAL STUDY OF THE PROPERTIES OF ALKALI METALS AND ALLOYS IN THE TEMPERATURE RANGE 1000-1800°K

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New apparatus for experimental study of the speed of sound and density of alkali metals in the fused state is described. Experimental data on saturated vapor pressure of the sodium—potassium eutectic are presented.

Possible applications of alkali metals and their alloys in a number of new branches of science and technology have stimulated the study of these materials' properties. Certain successes have been achieved in this field, although studies have more often been performed in an arbitrary fashion, over narrow temperature intervals. There is an especially severe lack of information on alkali metal alloys, interest in which has increased in recent years because of nuclear power generation applications [1]. Below we will describe equipment developed by us for study of the thermodynamic properties of alkali metals and their alloys.

Figure 1 is a schematic diagram of the equipment used for study of the speed of sound and p_sT_s and pVT properties of alkali metals and their alloys. It is based on working chamber 3 (a constant-volume piezometer) and measurement cell, the sensitive element of which is membrane 6, with registration being performed by inductive sensor 7. Working chamber 3, formed from niobium by electron beam fusion, is a closed vessel of constant volume, composed of eight coaxial cylinders welded to each other by electron beam welding and serving as an acoustical delay line.

There are connecting pipes above and below the chamber, by means of which the working chamber is connected to the membrane section using a niobium capillary and special gasketing. Niobium soundguides 1, 2 enter the chamber coaxially, and are located in a manner such that in one working position it is possible to measure the speed of sound in metal vapor, while

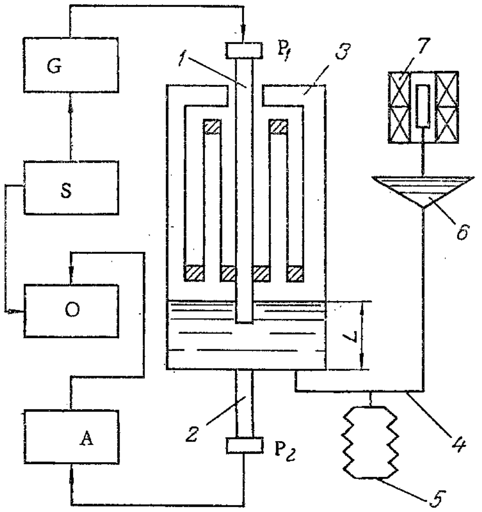

Fig. 1. Schematic diagram of equipment for speed of sound measurements.

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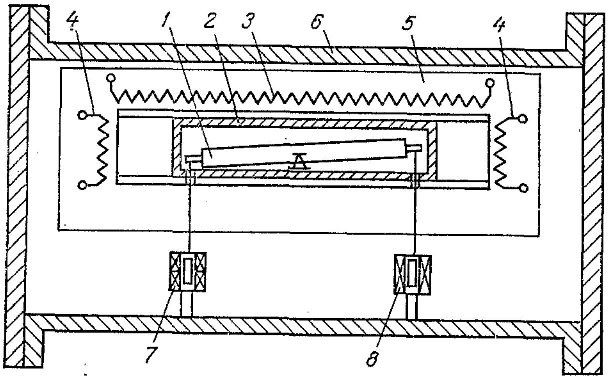

Fig. 2. Diagram of device for density measurement on the phase equilibrium curve.

when the chamber is rotated 180° the speed of sound can be measured in the liquid phase. The soundguide construction permits removal of the piezotransducers P_1 and P_2 from the high-temperature region. Niobium was chosen for the construction because of its combination of high corrosion resistance, good acoustical properties, and high temperature strength. Temperature was measured by PR 30/6 thermocouples, individually calibrated at reference points. The speed of sound was determined by the single fixed-distance pulse method. Generator G is triggered by the synchronization generator S. The ultrasound oscillations of transducer P_1 traverse the soundguide 1, the medium under study (a fixed length), and soundguide 2, whereupon they are converted to electrical signals by transducer P_2. The electrical signals are amplified by amplifier A and applied to the vertical input of oscilloscope O, the horizontal sweep of which is synchronized to the repetition rate of the probe pulses. The ultrasound pulse reflected from the face of the lower soundguide, having traversed a distance 2L in the medium under study, also reaches the oscilloscope vertical input. The speed of sound is then determined from the formula

$$V = \frac{2L}{\Delta\tau}. \tag{1}$$

Thus, the problem of the speed of sound determination reduces to determination of the time interval between the direct and reflected pulses. A type 15-27A generator is used to determine this interval. The distance involved can be determined quite accurately by calibrating the chamber with an inert gas, the speed of sound in which is known to the required accuracy.

To measure vapor pressure of the material under study, a variant of the static method is used, which eliminates direct contact of the inert gas with the substance and allows control of temperature stability of the gases under thermodynamic equilibrium conditions. To ensure a uniform temperature field over chamber height, the chamber is placed within a thermostatic volume. A system of heaters and thermal screens is used for the same purpose. Heating is performed by the electrical resistance furnace described in [2]. The vapor pressure arising within the chamber due to heating of the substance is transmitted by connector capillary 4 to the pressure measurement unit. The increase in pressure causes a change in the position of membrane 6, which is fixed by the indication of the inductive sensor 7. Application of a compensating external pressure causes the membrane to return to its initial state. At this moment, when the membrane is in the "zero" position, the external compensating pressure is equal to the vapor pressure of the material under study.

By measuring the compensating pressure and the temperature, we obtain the p_s—T_s curve of the material. Knowing the volume of the working chamber (determined beforehand by weighing the piezometer empty and filled with distilled water), we change the quantity of material in the chamber with feed device 5 and repeat the above procedure to obtain the pVT dependence of the material.

A unique feature of the apparatus described is that in one and the same chamber filling it is possible to measure the speed of sound in the liquid or gas phase and simultaneously measure the pVT properties and vapor pressure above the surface of the liquid phase, which is very important in calculating the thermophysical properties of the materials.

TABLE 1. Saturated Vapor Pressure of Sodium—Potassium Eutectic

No.	T, °K	$p^{expt} \cdot 10^{-5}$, N/m^2	$P^{calc} \cdot 10^{-5}$, N/m^2
		Series 1	
1	976,30	0,4411	0,4440
2	978,70	0,4540	0,4562
3	990,20	0,5180	0,5179
4	990,70	0,5259	0,5207
5	1013,80	0,6668	0,6646
6	1014,50	0,6716	0,6694
7	1029,60	0,7839	0,7794
8	1030,90	0,7936	0,7895
9	1058,50	1,0292	1,0279
10	1059,00	1,0344	1,0326
11	1083,60	1,2879	1,2889
12	1084,60	1,2997	1,3003
13	1102,60	1,5158	1,5175
14	1103,60	1,5331	1,5304
15	1111,90	1,6395	1,6399
16	1113,40	1,6586	1,6603
17	1126,30	1,8456	1,8438
18	1134,50	1,9655	1,9681
19	1135,70	1,9826	1,9868
20	1153,00	2,2745	2,2713
21	1153,40	2,2817	2,2782
22	1165,50	2,4971	2,4949
23	1187,00	2,9124	2,9174
24	1188,00	2,9321	2,9383
25	1199,80	3,1969	3,1927
26	1215,40	3,5493	3,5538
27	1216,10	3,5689	3,5707
28	1224,20	3,7650	3,7703
29	1239,50	4,1574	4,1697
30	1249,20	4,4320	4,4387
31	1263,40	4,8243	4,8551
32	1305,20	6,2317	6,2492
33	1306,80	6,2954	6,3078
		Series 2	
34	962,10	0,3766	0,3733
35	1006,80	0,6209	0,6181
36	1012,40	0,6589	0,6551
37	1012,80	0,6637	0,6578
38	1022,90	0,7334	0,7290
39	1024,10	0,7427	0,7379
40	1037,50	0,8509	0,8421
41	1038,70	0,8629	0,8521
42	1062,00	1,0683	1,0616
43	1078,60	1,2415	1,2340
44	1100,00	1,4957	1,4846
45	1100,60	1,5033	1,4921
46	1109,40	1,6181	1,6063
47	1121,20	1,7808	1,7695
48	1121,70	1,7896	1,7767
49	1135,00	1,9881	1,9758
50	1153,60	2,2925	2,2816
51	1156,10	2,3401	2,3253
52	1157,60	2,3708	2,3518
53	1167,80	2,5613	2,5378
54	1168,30	2,5710	2,5472
		Series 3	
55	1015,30	0,6758	0,6749
56	1053,80	0,9869	0,9839
57	1088,90	1,3589	1,3499
58	1090,90	1,3812	1,3734
59	1124,70	1,8043	1,8203
60	1133,30	1,9471	1,9494
61	1135,70	1,9895	1,9867
62	1146,40	2,1400	2,1610
63	1158,40	2,3678	2,3680
64	1159,30	2,3811	2,3820
65	1161,70	2,4455	2,4253
66	1162,70	2,4466	2,4435
67	1166,80	2,5079	2,5191
68	1170,10	2,5727	2,5812
69	1177,50	2,6960	2,6155
70	1220,90	3,6774	3,6880
71	1233,30	4,0080	4,0042

TABLE 1 (continued)

No.	T, °K	$p^{expt}\cdot 10^{-5}$ N/m^2	$p^{calc}\cdot 10^{-5}$ N/m^2
		Series 3 (continued)	
72	1233,90	4,0275	4,0200
73	1262,60	4,8641	4,8309
74	1266,40	4,9720	4,9466
75	1293,00	5,8547	5,8152
76	1333,10	7,3750	7,3313
77	1370,70	9,0422	9,0026
		Series 4	
78	965,40	0,3889	0,3921
79	1009,00	0,6357	0,6324
80	1055,30	0,9991	0,9977
81	1090,70	1,3701	1,3710
82	1136,00	1,9762	1,9914
83	1147,40	2,1657	2,1760
84	1166,50	2,5111	2,5135
85	1186,50	2,9074	2,9069
86	1214,10	3,5419	3,5226
87	1252,20	4,5158	4,5243
88	1274,50	5,2122	5,2002
89	1299,20	5,9674	6,0328
90	1326,30	7,0462	7,0557
91	1338,80	7,5856	7,5684
92	1359,00	8,4880	8,4550
93	1369,50	8,9587	8,9453
94	1387,50	9,8218	9,8347
95	1398,40	10,3710	10,4040
96	1414,30	11,2430	11,2800
97	1427,90	12,0380	12,0710
98	1444,10	13,0870	13,0690

Figure 2 shows a diagram of the device used for measuring the density of alkali metal vapor and liquid on the phase equilibrium curve. Measurements are performed as follows [3]. The thin-wall hermetic tube 1, made of a refractory metal (molybdenum, tantalum, niobium), is mounted on sapphire needle bearings and acts as a scale balance beam. The plungers of the inductive differential displacement sensor 7 and solenoid 8 are attached to the ends of the tube. The tube is then balanced in a position several degrees away from the horizontal using nuts installed on the ends of the tube. The slant of the tube is adjusted so that after it is installed within thermostat 2 the end connected to the sensor plunger will rest on the bottom of the chamber. The tube is then filled with a certain quantity of the material, the mass of which is determined by weighing, and sealed. The tube is placed within the thin-wall molybdenum thermostat chamber, and the liquid settles at the end connected to the displacement plunger. Heating is performed by main heater 3 and two end heaters 4, permitting maintenance of a temperature differential between the midpoint and ends of the chamber of not more than 1°K. Type PR 30/6 thermocouples are used for temperature measurement. Each thermocouple is individually calibrated at the melting points of sulfur, silver, gold, platinum, and palladium. The heaters are surrounded by a complex system of radiation screens 5. During the heating process the value of the smallest current in the solenoid winding which will move the tube from its original position is determined by a galvanometer connected in a bridge circuit within the displacement sensor circuit. It is obvious that as temperature is increased the material evaporates within the tube and the required current in the solenoid winding will decrease. At some temperature the decrease in current will stop, indicating that all the material is in a single phase. When the mass of the submerged material is less than the critical value, at this temperature the entire tube will be filled with vapor, or when the mass is above the critical value, the tube will be filled by liquid. The density is calculated by using the mass of the submerged material and the previously calculated tube volume. Subsequent increase in the mass of material used permits study of the dependence of vapor and liquid density on the phase equilibrium curve upon temperature, as well as measurement or estimation of the critical density and temperature of the material. To increase the sensitivity of the technique, the tube used is thin-wall and is protected from bursting by application of a compensating inert gas pressure from the high-pressure shell 6.

Using the apparatus described in detail in [2], the saturated vapor pressure of the sodium—potassium eutectic was measured by the static method. The alloy studied was prepared by the Institute for the Chemistry and Technology of Rare Elements and Minerals of the Kola Branch of the Academy of Sciences of the USSR. The alloy was placed in glass ampuls 50 cm^3 in volume sealed under vacuum. The labeled composition of the alloy was: Na, 22.8; K, 77.2 wt. %. Uncertainty in determination of the composition did not exceed ±0.2 wt.%. Data of a chemical analysis of the components (sodium and potassium) for metallic and gaseous impurities indicated a purity of 99.995%.

The operating chamber was filled under a vacuum of 10^{-4} mm Hg or better. Four series of measurements were performed in the temperature range 962-1444°K. Results are presented in Table 1.

The uncertainty of the experiment, including systemic and random components, was calculated by the method described in [4] for the 0.95 confidence level. Its average value over the temperature range studied was 1.5%, with analysis revealing that its major component is reference error.

The data obtained were processed by the least-squares method on a BÉSM-4 computer using the method of [5]. The optimum number of parameters for the approximating equation was found with Fisher's criterion. The equation had the form

$$\ln p_s = 26.0664 - \frac{22.6895}{\tau} - 19.6535 \ln \tau + 7.5832\tau, \qquad (2)$$

where p_s is the pressure of the saturated vapor of the sodium—potassium eutectic in N/m^2, T is the MPTSh-68 temperature, and $\tau = T/1000$.

The mean-square deviation of the experimental points from the approximate equation does not exceed 0.5%. A comparison of the data obtained with those of other authors [6] showed satisfactory agreement within the limits of experimental error.

To verify the applicability of Raul's law in the temperature interval studied for the sodium—potassium eutectic, the experimental data were compared to data obtained by calculation with the values of the saturated vapor pressures of sodium and potassium. The initial data used were vapor tension values for sodium and potassium from [7-9], which we feel to be some of the most reliable experimental data available. It was thus established that the data of the present study lie 3.5-2.0% above the calculated values, with the difference decreasing with increase in temperature.

NOTATION

p_s, saturated vapor pressure; T_s, saturation temperature; V, speed of sound; L, calibrated distance between faces of soundguides; $\Delta\tau$, time required for transit of ultrasound pulse through distance 2L.

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GENERAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF ALKALINE EARTH METALS

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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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