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EQUATION OF STATE OF THE LIQUID ALKALI METALS. I.

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Experimental PVT data are given for sodium, rubidium, and cesium in the liquid phase. Procedures and measurement errors are discussed.

Introduction. The liquid alkali metals, in view of the relative simplicity of their structure, can serve as reference items for studying the liquid metal state of a substance. On the other hand, no doubts arise concerning the great prospects for using these metals in various fields of new technology, including their use as coolants.

However, despite the considerable interest which has been shown in recent years toward liquid metals in general, and to the alkali metals in particular [1-3], up to the present time their fundamental characteristics such as the equation of state and its derivatives – compressibility and thermal expansion – remain very little studied.

For the alkali metals in the liquid phase, the temperature range of reliable PVT data is limited, in practice, to 200°C [4-7]. The main quality of data about the thermophysical properties of the fused metals of the first group refers to the line of saturation [8, 9]. In the single-phase region, in addition to the papers mentioned above, PVT data exist on potassium at pressures up to 100 atm and temperatures up to 2050°K [10], also on rubidium in the temperature range 300-1400°C and pressures up to 400 bar [11]. Data exist for cesium on density, obtained by a radioactive method, over a wide range of parameters of state ($P \leq 600$ atm, $600°C \leq T \leq 2500°C$) [12, 13].

The present paper is devoted to an experimental study of the equation of state of liquid cesium, rubidium, and sodium, in the temperature range 500-1000°K and pressures up to 750 atm for cesium and rubidium, and up to 500 atm for sodium.

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TABLE 1. Experimental Data on the Density of Liquid Sodium

P, kgf/cm²	ρ, g/cm³	T, °K	P, kgf/cm²	ρ, g/cm³	T, °K	P, kgf/cm²	ρ, g/cm³	T, °K
12	0,870	613,6	98,5	0,830	790,2	220	0,808	897,0
12	0,860	654,4	98,5	0,815	858,1	220	0,800	930,0
12	0,851	693,4	98,5	0,808	884,0	220	0,792	972,8
12	0,845	722,4	98,5	0,806	896,7	219	0,779	1019,7
12	0,836	759,6	98,5	0,798	927,5			
12	0,816	841,7	98,5	0,787	973,2	470	0,890	570,2
12	0,809	868,1	98,5	0,780	1002,0	470	0,880	608,9
12	0,800	906,0				470	0,865	679,0
12	0,789	956,4	220	0,881	585,7	471	0,845	763,7
12	0,779	998,9	220	0,872	623,1	471	0,839	790,5
			220	0,859	680,6	470	0,828	838,1
98,5	0,868	631,6	217	0,841	757,2	470	0,818	883,2
97	0,858	675,3	218	0,834	784,2	470	0,809	918,2
98,5	0,850	711,1	220	0,825	828,2	470	0,799	961,1
98,5	0,842	744,7	219	0,816	864,2	470	0,789	1007,2
						470	0,781	1041,4

Experimental Procedure and Measurement Errors

The measurements were carried out by a dilatometric method. The dilatometer was a cylindrical cell of stainless steel with a volume of 10 cm³, joined to a glass measurement tube by a fine steel capillary, with contacts by the closure of which the level of the expanded metal was determined. The volume of the cell and the measurement tube was carefully calibrated with water and mercury, respectively.

The dilatometer, charged with the metal being investigated, was placed in a high-pressure autoclave, which was divided into two thermostatically controlled zones cooled by a partition (baffle). The measurement tube of the dilatometer was located in the upper cold zone of the autoclave, at a temperature 10-20°K higher than the melting point of the metal being investigated. In the lower, hot zone, the steel cell of the dilatometer was located and was heated by a graphite heater. The maximum temperature spread over the cell with the metal did not exceed 2°K in our experiments. The calculation of the thermal expansion of the dilatometer cell was carried out by the well-known formula, with the coefficient of thermal expansion of stainless steel taken from [14].

Purified argon was used as the pressurizing medium.

Detailed diagrams and a description of the facility for the experimental investigation of the equation of state of the liquid alkali metals are given in [15].

The measurements were conducted at constant pressure, so that during the experiment both the temperature and pressure were maintained constant in the cold measurement zone of the autoclave.

One charge was used on each isobar and, consequently, the level of the metal each time was raised through a clean tube.

The calculation of the compressibility and thermal expansion of the alkali metals in the cold zone was carried out by the appropriate data of [5, 6].

The principal sources of error in the data obtained for the density of liquid sodium, rubidium, and cesium are as follows: the error in measuring the volume of the dilatometer, taking account of the presence of a meniscus in the tube (0.08%); the error in measuring the volume of the dilatometer, taking account of the density determination of the metal in the capillary of the dilatometer (0.05%), and the error due to the temperature spread over the dilatometer cell (0.06%).

Taking into account other measurement errors, such as the error in measuring the temperature and pressure, which are attributed to a reference error ($\leqslant 2\cdot10^{-3}$%); the error due to inaccuracy of the literature data, by which the compressibility and thermal expansion of the alkali metals in the cold zone and the thermal expansion of the dilatometer were taken into account ($\leqslant 1\cdot10^{-2}$%), and the error in determining the mass of the metal charge ($\leqslant 10^{-3}$%), the error in measuring the density of the liquid alkali metals in our experiments did not exceed 0.2%.

The solubility of argon in the alkali metal can also contribute a finite error to the data obtained. In our experiments, the compressed argon and the fused metal being investigated are in direct contact in the measurement tube, where they are maintained at constant pressure and temperature during the experiment.

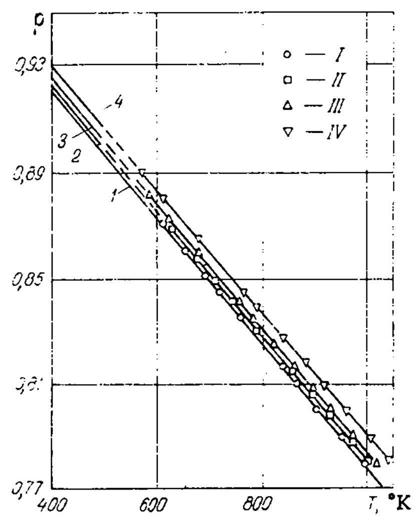

Fig. 1

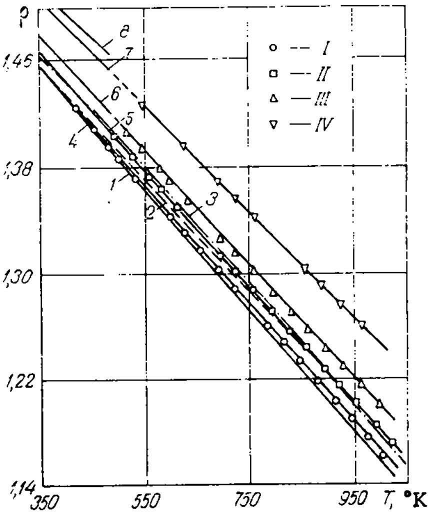

Fig. 2

Fig. 1. Density of liquid sodium: 1) line of saturation [8, 9]; 2-4) isobars for P = 92.5, 220, and 470 kgf/cm^2 [4, 5], respectively; authors' data: I) P = 12 kgf/cm^2; II) 92.5; III) 220; IV) 470. ρ, g/cm^3; T, °K.

Fig. 2. Density of liquid rubidium: 1-3) line of saturation [9, 19, 20], respectively; 4-7) isobars for P = 11, 150, 300, and 750 kgf/cm^2, respectively, recalculated by the data of [6, 7], and tied into the line of saturation [9]; 8) isobar for P = 750 kgf/cm^2 [6]; authors' data: I) P = 11 kgf/cm^2; II) 150; III) 300; IV) 750. ρ, g/cm^3; T, °K.

We can make some estimate of the effect of solubility from a comparison of our data with the experimental data, where solubility is excluded. This involves the PVT measurement results of sodium and cesium, carried out at the Institute of Crystallography of the Academy of Sciences of the SSSR by the piston piezometer method [4, 5]. The comparison carried out below does not indicate a marked effect of solubility on our measurement results. A quantitative estimate of the error in our data due to solubility also confirms this.

The data known to us concerning the solubility of argon, R, in the liquid alkali metals, refer mainly to sodium [16-18], and therefore in the quantitative estimate of the effect of solubility we must confine ourselves to this metal. According to the data of [16-18], the solubility of argon in liquid sodium is 10^{-12} to 10^{-13} parts by weight at a temperature of 100°C.

In [18], there are data concerning the dependence of the solubility of argon in liquid sodium on the pressure for $0 < P \leq 9$ atm. A proportionality between R and P is noted, which agrees with Henry's law. By roughly extrapolating this dependence to pressures of 500 atm, we obtain the upper limit of the quantity R = 10^{-2}-10^{-11} parts by weight.

It is obvious that the volume of sodium in which the argon is dissolved does not exceed the volume in which the argon diffuses during the experiment. This volume is determined by the area of the content surface of the argon with the sodium (cross-sectional area of the measurement tube) and the diffusion length $L = \sqrt{Dt}$, where D is the coefficient of diffusion and t is the time during which a single experiment is conducted (5 h).

There are data in [16] for D at normal pressure. As it is well known that the coefficient of diffusion in any cases does not increase with increase of pressure, then it is obvious that the value of D from [16] can be used as the upper limit of the coefficient of diffusion in the case of increased pressure. This value, according to [16], is equal to $4 \cdot 10^{-5}$ cm^2/sec.

Thus, with t = 5 h, $D = 4 \cdot 10^{-5}$ cm^2/sec, and $R = 10^{-11}$ g/g, the maximum change of volume of the melt due to solubility of argon was obtained, $\Delta V = 10^{-12}$ cm^3. It is obvious that this quantity is very small.

PVT Measurement Results for Sodium, Rubidium, and Cesium in the Liquid Phase

In the present series of experiments, the procedure described has been used for PVT measurements of liquid sodium, rubidium, and cesium.

TABLE 2. Experimental Data on the Density of Liquid Rubidium

P, kgf/cm^2	ρ, g/cm^3	T, °K	P, kgf/cm^2	ρ, g/cm^3	T, °K	P, kgf/cm^2	ρ, g/cm^3	T, °K
11	1,424	419,8	150	1,37	561,9	300	1,315	723,9
11	1,409	452,4	150	1,364	581,8	301	1,301	758,5
11	1,396	480,4	150	1,350	613,1	300	1,285	794,4
11	1,386	501,9	150	1,314	695,2	301	1,270	831,5
11	1,372	533,0	150	1,302	723,2	301	1,257	861,8
11	1,343	600,0	150	1,288	757,7	300	1,243	897,1
11	1,332	625,1	150	1,272	793,7	299	1,230	927,6
11	1,318	657,4	150	1,257	826,2	300	1,216	962,8
11	1,303	691,5	150	1,244	858,2	300	1,200	995,8
11	1,288	721,8	150	1,228	891,7			
11	1,260	783,5	151	1,216	920,7	750	1,427	546,1
11	1,248	814,7	150	1,202	951,6	753	1,396	622,9
11	1,234	844,3	150	1,186	988,7	751	1,382	655,2
11	1,219	879,1	150	1,172	1023,2	750	1,369	689,1
11	1,203	914,7				750	1,356	720,7
11	1,190	943,7	300	1,406	516,1	751	1,343	761,3
11	1,176	974,8	300	1,393	543,2	756	1,304	857,2
11	1,162	1003,4	300	1,379	577,7	750	1,292	886,0
			300	1,370	596,0	750	1,277	922,1
151	1,403	493,7	300	1,354	633,2	750	1,261	963,4
150	1,388	526,0	300	1,326	697,5			

For sodium, the measurements were conducted at pressures of 12, 98.5, 220, and 470 kgf/cm^2, and a total of 43 experimental points were obtained (Table 1 and Fig. 1). The purity of the sodium investigated amounted to 0.9999.

In Fig. 1, the literature data for the density of liquid along the line of saturation [9] are shown in addition to our data. In the single-phase region, PVT data for liquid sodium are available in the temperature range up to 220°C and for pressures up to 22 kbar [4]. The excellent agreement between our PVT data for liquid sodium and the data of other authors can be seen from the figure.

Density measurements for fused rubidium were carried out for pressures of 11, 150, 300, and 750 kgf/cm^2, and a total of 59 experimental points were obtained (Table 2 and Fig. 2). The purity of the rubidium was 0.9995.

In Fig. 2, in addition to our data, the literature data are given for the density of liquid rubidium along the line of saturation [9, 19, and 20], which differ significantly from one another ($\simeq$ by 2% at 1000°K), and the authors' estimates of the errors in them amount to 0.5-1%. Our data for the density at low pressures ($P = 10$ atm) are located close to the line of saturation given in the monograph [9].

In the single-phase region of liquid rubidium, PVT data are available, obtained in [6, 7] over the temperature range up to 200°C and pressures up to 1380 bar. It can be seen from Fig. 2 that when they are tied into the line of saturation [9], which in this region is close to our data, they agree well between themselves and with the extrapolated parts of our isobars. The point is that in [6], the data on the density of liquid rubidium were calculated by the method of iteration based on measurements of the velocity of sound carried out in [6], using the data for the density ρ, thermal expansion α, and the isobaric specific heat C_p from [20]. An equation of state is derived in [7], in which the absolute volume of a sample of liquid rubidium is expressed as a function of the pressure and temperature.

In [11] the results are given of the measurement of the density, conductivity, and thermal emf of liquid at temperatures from 300 to 1400°C and pressures of up to 400 bar. The change of volume of a sample of liquid rubidium was measured with high accuracy (0.2%). The density was calculated using the literature data for the line of saturation. The total error on the density in [11] amounts to 2.5%. Unfortunately, all the data here about the equation of state is only shown graphically. A comparison shows that the isothermic changes of density in [11] agree well with the same quantities obtained from our data.

The PVT measurements of liquid cesium were conducted at pressures of 10, 155, 300, and 735 kgf/cm^2, and a total of 61 experimental points were obtained (Table 3, Fig. 3). The purity of the cesium was 0.9999.

Figure 3 shows the data for the density along the line of saturation from [9] and in the single-phase region from [5], in which the range of measurements was up to 220°C and 18 kbar. It can be seen from the figure that at low pressures our data agree well with the results on the line of saturation [9]. In the single-phase region, the extrapolated parts of the isobars differ from the corresponding values of [5] by not more

TABLE 3. Experimental Data on the Density of Liquid Cesium

P, kgf/cm²	ρ, g/cm³	T, °K	P, kgf/cm²	ρ, g/cm³	T, °K	P, kgf/cm²	ρ, g/cm³	T, °K
10	1,801	367,3	155	1,697	586,5	300	1,707	607,8
10	1,782	397,6	155	1,686	606,4	301	1,687	645,3
10	1,764	430,8	155	1,668	639,1	300	1,666	687,3
10	1,745	461,8	155	1,655	662,3	300	1,651	712,4
10	1,731	489,0	155	1,640	690,2	300	1,637	740,1
10	1,716	516,6	155	1,627	711,0	300	1,616	776,7
10	1,697	548,1	155	1,609	745,2	300	1,600	805,9
10	1,680	576,5	155	1,568	820,1	300	1,580	846,6
10	1,663	609,6	155	1,629	710,6	302	1,563	877,0
10	1,643	644,3	155	1,613	739,1	300	1,546	912,0
10	1,624	676,9	155	1,596	769,9	300	1,494	1007,3
10	1,607	705,0	157	1,577	803,5			
10	1,572	766,8	155	1,523	902,4	735	1,779	582,0
10	1,556	796,3	155	1,501	942,4	735	1,768	603,8
10	1,515	870,5	156	1,484	973,6	734	1,750	639,3
10	1,503	891,5	155	1,470	988,5	736	1,709	727,5
10	1,480	929,7	155	1,460	1016,6	735	1,669	805,4
10	1,455	975,3	157	1,434	1064,1	735	1,614	918,6
10	1,438	1003,0				735	1,596	960,5
			300	1,765	496,1	735	1,580	991,7
155	1,775	444,5	301	1,749	529,2			
156	1,756	478,1	300	1,724	575,0			

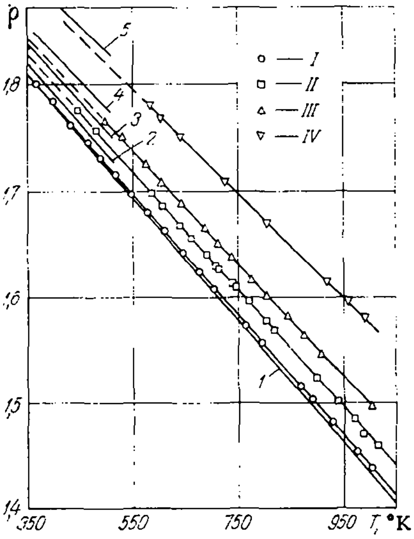

Fig. 3. Density of liquid cesium: 1) line of saturation [9]; 2-5) isobars for P = 10, 155, 300, and 735 kgf/cm² [5]; authors' data: I) P = 10 kgf/cm²; II) 155; III) 300; IV) 735, ρ, g/cm³; T, °K.

than 0.5%. It should be noted that for the saturation line the density data of [5] differ somewhat from the density data of [9] on the saturation line. When the results of [5] are tied into the line of saturation [9], the deviation between the extrapolated values of our measurements and the data of [5], corrected in this way, does not exceed 0.15%.

The equations of state of the metals investigated were conducted from the measurements results given, in analytic form, and will be presented in our next paper.

NOTATION

P	is the pressure;
V	is the volume;
T	is the temperature;
ρ	is the density;
R	is the solubility;

D is the coefficient of diffusion;
t is the time;
L is the diffusion length;
α is the thermal expansion;
C_p is the isobaric specific heat.

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