AN EXPERIMENTAL STUDY OF THE EQUATIONS OF STATE OF LIQUID ALKALI METALS. II

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Equations of state are presented in analytic form for liquid sodium, rubidium, and cesium, as obtained from experimental PVT data.

The present authors with collaborators have previously presented [1] results of experiments on PVT curves of liquid sodium, rubidium, and cesium. Measurements were performed by the dilatometric method [2] at temperatures from 500 to 1000°K and pressures up to 500 atm for sodium and 750 atm for rubidium and cesium. The error in the PVT data obtained does not exceed 0.2% with respect to density for all the metals. The present study will offer equations of state for the metals studied based on the experimental data obtained in [1]. The form of the equations selected was the following:

$$P = \sum_{i,j} A_{ij} \rho^i T^j, \tag{1}$$

where P is pressure, Pa; ρ, density, kg/m^3; T, temperature, °K; A_{ij}, polynomial coefficients, chosen by the least-squares method. The equations of state thus obtained were used to compile detailed PVT tables describing the properties of sodium, rubidium, and cesium, which are presented below;

Sodium. Equation of state (1) approximating the PVT data obtained for liquid sodium [1] has the coefficients shown in Table 1.

The mean-square error in the approximation comprises 13.5 bar, which corresponds to a deviation of experimental density values from calculated values of $<0.04\%$, i.e., less than the error of the experimental data (0.2%).

The proposed equation of state for liquid sodium is applicable over a temperature range from 500 to 1000°K and from the saturation pressure P_s to 500 bar.

TABLE 1. Coefficients A_{ij} of Eq. (1) for Liquid Sodium

j	i		
	0	1	2
0	$0{,}759850 \cdot 10^{10}$	$-0{,}217659 \cdot 10^{8}$	$0{,}140684 \cdot 10^{5}$
1	$-0{,}173184 \cdot 10^{7}$	$0{,}328027 \cdot 10^{4}$	—

TABLE 2. Density of Liquid Sodium, $\rho \cdot 10^{-3}$, kg/m^3 at T, °K

$P \cdot 10^{-5}$, Pa	500	600	700	800	900	1000
P_s	0,897	0,873	0,850	0,826	0,802	0,778
100	0,899	0,875	0,852	0,828	0,805	0,781
200	0,901	0,877	0,854	0,831	0,807	0,784
300	0,903	0,879	0,856	0,833	0,810	0,786
400	0,905	0,881	0,858	0,835	0,812	0,789
500	0,906	0,883	0,860	0,837	0,814	0,792

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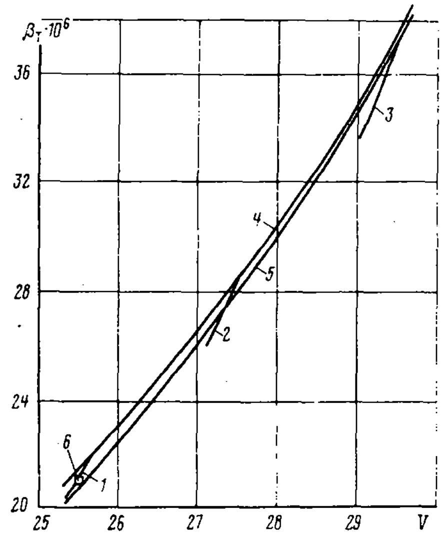
TABLE 3. Pressure, Pa; Isothermal Compressibility, β_T, Pa^{-1}; and Thermal Expansion α_p, °K^{-1}, of Liquid Sodium at Various Molar Volumes V, m^3/kmole, and Temperatures T, °K

$V\cdot10^3$	500			600			700		
	$P\times10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\times10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\times10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$
25,5	229,1	21,2	2,59						
26				531,3	22,2	2,60			
26,25				113,4	23,6	2,69			
26,75							445,3	24,7	2,68
27							79,3	26,2	2,78
27,5									
27,75									
28,25									
28,5									
29,25									
29,5									

$V\cdot10^3$	800			900			1000		
	$P\times10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\times10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\times10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$
25,5									
26									
26,25									
26,75									
27									
27,5	428,6	27,3	2,76						
27,75	106,7	28,9	2,85						
28,25				463,4	30,1	2,82			
28,5				179,0	31,9	2,92			
29,25							282,4	35,0	2,97
29,5							46,9	37,3	3,07



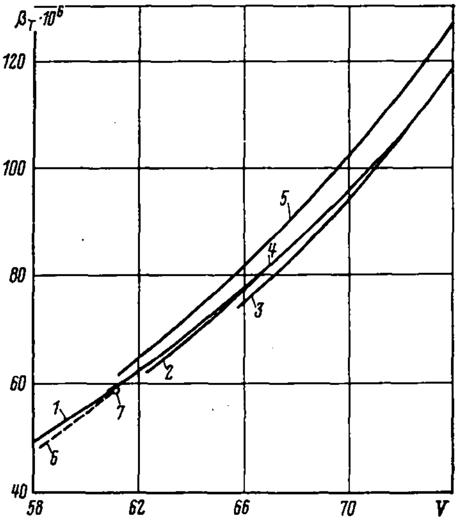


Fig. 1 Fig. 2

Fig. 1. Isothermal compressibility of liquid sodium: 1) T = 500°K; 2) 750; 3) 1000; 4) β_T along saturation line; 5) β_T along saturation line [3]; 6) β_T at 493.15°K [4]. $\beta_T\cdot10^6$, bar^{-1}; V, cm^3/mole.

Fig. 2. Isothermal compressibility of liquid rubidium: 1) T = 500°K; 2) 750; 3) 1000; 4) β_T along saturation line; 5) β_T along saturation line [7]; 6) β_T at 473.15°K [5]; 7) β_T along saturation line at 473.15°K [6].

The smoothed values of density ρ presented in Table 2 were calculated from the equation of state thus obtained, together with values of pressure P, isothermal compressibility $\beta = -V^{-1}(\partial V/\partial P)_T$ and coefficient of thermal expansion $\alpha_p = V^{-1}(\partial V/\partial T)_p$ (Table 3).

Figure 1 shows three curves of the isothermal compressibility of liquid sodium. Curve 4 shows compressibility along the saturation line ($P = P_s$). For comparison, also shown are the compressibility

TABLE 4. Coefficients A_{ij} of Eq. (1) for Liquid Rubidium

i	j = 0	1	2
0	—	$0,551572\cdot10^6$	$-0,171719\cdot10^3$
1	$-0,133705\cdot10^7$	$0,110035\cdot10^3$	—
2	$0,626332\cdot10^3$	—	—
3	$0,127431\cdot10^0$	—	—

TABLE 5. Density of Liquid Rubidium $\rho\cdot 10^{-3}$, kg/m^3, at T, °K

$P\cdot10^{-5}$, Pa	500	600	700	800	900	1000
P_s	1,387	1,342	1,298	1,253	1,207	1,162
100	1,395	1,351	1,308	1,264	1,219	1,176
200	1,404	1,360	1,318	1,274	1,231	1,189
300	1,412	1,369	1,327	1,284	1,242	1,204
400	1,420	1,378	1,336	1,294	1,253	1,212
500	1,428	1,386	1,345	1,303	1,263	1,224
600	1,435	1,394	1,354	1,313	1,274	1,235
700	1,423	1,402	1,362	1,322	1,284	1,246
800	1,450	1,410	1,371	1,332	1,294	1,257
900	1,458	1,418	1,379	1,341	1,304	1,267
1000	1,465	1,426	1,387	1,350	1,313	1,277

TABLE 6. Pressure P, Pa; Isothermal Compressibility β_T, Pa^{-1}; and Thermal Expansion α_p, °K^{-1}, of Liquid Rubidium at Various Molar Volumes V, m^3/kmole, and Temperatures T, °K

$V\cdot10^3$	500			600			700			800			900			1000		
	$P\cdot10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\cdot10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\cdot10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\cdot10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\cdot10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$	$P\cdot10^{-5}$	$\beta_T\cdot10^{11}$	$\alpha_p\cdot10^4$
59	774,2	51,7	2,79															
60	458,8	54,9	2,95	978,2	54,5	2,73												
61	166,7	58,3	3,11	683,5	57,8	2,89												
62				410,4	61,4	3,05	890,5	60,8	2,81									
63				157,2	65,1	3,22	634,9	64,5	2,97									
64							397,7	68,4	3,13	838,6	67,7	2,87						
65							177,6	72,6	3,31	616,3	71,8	3,03						
66										409,8	76,1	3,19	811,9	75,3	2,90			
67										217,9	80,7	3,37	617,9	79,8	3,06	983,6	78,9	2,75
68										39,7	85,6	3,55	437,6	84,6	3,22	801,2	83,6	2,90
69													279,0	89,7	3,40	631,6	88,6	3,05
70													114,1	95,1	3,58	473,8	93,9	3,21
71																327,0	99,5	3,39
72																257,5	105,5	3,57
73																63,4	111,8	3,77

TABLE 7. Coefficients A_{ij} of Eq. (1) for Liquid Cesium

i	j = 0	1	2
0	—	$0,386907\cdot10^6$	$-0,116060\cdot10^3$
1	$-0,802537\cdot10^6$	$0,731417\cdot10^2$	—
2	$0,315008\cdot10^3$	—	—
3	$0,429652\cdot10^{-1}$	—	—

TABLE 8. Density of Liquid Cesium, $\rho\cdot10^3$, kg/m^3, at T, °K

$P\cdot10^{-5}$, Pa	500	600	700	800	900	1000
P_s	1,723	1,667	1,610	1,552	1,494	1,435
100	1,738	1,682	1,627	1,570	1,514	1,457
200	1,752	1,697	1,643	1,588	1,533	1,479
300	1,765	1,711	1,659	1,605	1,552	1,499
400	1,778	1,725	1,674	1,621	1,570	1,519
500	1,791	1,739	1,688	1,637	1,587	1,537
600	1,804	1,753	1,703	1,652	1,603	1,555
700	1,817	1,766	1,717	1,667	1,619	1,572
800	1,829	1,779	1.730	1,682	1,635	1,589
900	1,841	1,792	1,743	1,696	1,651	1,606
1000	1,854	1,805	1,756	1,711	1,666	1,622

TABLE 9. Pressure P, Pa; Isothermal Compressibility β_T, Pa^{-1}; and Thermal Expansion α_p, $°K^{-1}$, of Liquid Cesium at Various Molar Volumes V, m^3/kmole, and Temperature T, °K

$V \cdot 10^3$	500			600			700			800			900			1000		
	$P \cdot 10^{-5}$	$\beta_T \cdot 10^{11}$	$\alpha_p \cdot 10^4$	$P \cdot 10^{-5}$	$\beta_T \cdot 10^{11}$	$\alpha_p \cdot 10^4$	$P \cdot 10^{-5}$	$\beta_T \cdot 10^{11}$	$\alpha_p \cdot 10^4$	$P \cdot 10^{-5}$	$\beta_T \cdot 10^{11}$	$\alpha_p \cdot 10^4$	$P \cdot 10^{-5}$	$\beta_T \cdot 10^{11}$	$\alpha_p \cdot 10^4$	$P \cdot 10^{-5}$	$\beta_T \cdot 10^{11}$	$\alpha_p \cdot 10^4$
72	941,2	64,8	2,63															
73	733,3	67,9	2,74															
74	537,8	71,3	2,87	928,4	70,6	2,68												
75	353,8	74,7	2,99	742,6	74,0	2,79												
76	180,6	78,3	3,12	567,8	77,6	2,91	931,7	76,8	2,71									
77	17,6	82,1	3,26	403,1	81,3	3,04	765,4	80,5	2,82									
78				248,0	85,2	3,17	608,7	84,3	2,94	946,1	83,4	2,72						
79				101,9	89,2	3,31	461,0	88,3	3,07	796,8	87,3	2,83						
80							321,7	92,5	3,20	656,0	91,4	2,95	967,2	90,4	2,71			
81							190,4	96,8	3,33	523,2	95,7	3,07	832,8	94,6	2,82			
82							66,6	101,4	3,48	397,9	100,2	3,20	706,1	99,0	2,94	991,0	97,9	2,67
83										279,7	104,9	3,34	586,4	103,6	3,06	869,9	102,4	2,78
84										168,1	109,8	3,48	473,4	108,6	3,18	755,5	107,1	2,90
85										62,8	115,0	3,63	366,7	113,5	3,32	647,5	112,0	3,02
86													266,0	118,8	3,46	545,4	117,2	3,14
87													170,8	124,3	3,60	449,0	122,6	3,27
88													81,0	130,1	3,75	357,8	128,3	3,40
89																271,7	134,2	3,54
90																190,3	140,5	3,69
91																113,4	147,0	3,85
92																40,8	153,9	4,01

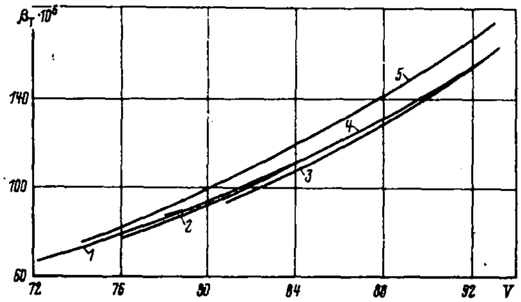


Fig. 3. Isothermal compressibility of liquid cesium: 1) T = 500°K; 2) 750; 3) 1000; 4) β_T along saturation line; 5) β_T along saturation line [9].

curve along the saturation line obtained by measurements of the speed of sound [3] (curve 5), and the value of β_T at 493.15°K and molar volume V = 25.5 cm^3/mole, taken from [4].

The maximum divergence of the compressibility values obtained from the proposed equation state from the data of [3] does not exceed 3% (in [3] the authors' estimate of error $\delta\beta_T = 3\%$), while the divergence of the present β_T data from corresponding values of [4] lies within the limits of 1%.

Rubidium. The coefficients of Eq. (1) approximating our experimental PVT data for rubidium in the liquid phase [1] are shown in Table 4.

The mean-square error of the approximation of the experimental data by the proposed equation comprises 10 bar, which corresponds to a discrepancy between experimental and calculated density values of not more than 0.08%.

As was demonstrated in [1], our density data at low temperatures, and thus, the density values calculated with Eq. (1), agree well with the data of Rosenbaum [5] and Jarzynski [6] over the pressure range studied (to 750 atm). Moreover, the same degree of agreement (within 0.2% in density) can be found in density values from Eq. (1) at higher pressures. Based on this fact, we can recommend the following range of applicability for Eq. (1) for liquid rubidium: pressures from P_s to 10^8 Pa (1000 bar), and temperatures from 500 to 1000°K.

Smoothed density values of liquid rubidium are presented in Table 5.

Table 6 presents values of pressure, isothermal compressibility, and thermal expansion of fused rubidium at various molar volumes and temperatures, as calculated from equation of state (1).

Figure 2 presents isothermal compressibility curves for three temperatures and along the saturation line. Curve 5 shows compressibility obtained from speed of sound measurements [7], with the authors' estimate of uncertainty in β_T measurements being 6%. The divergence of the present data from that of [7] does not exceed 9%. The isothermal compressibility curve shown in Fig. 2 for 200°C [5] differs from the compressibility values obtained with Eq. (1) by not more than 3%. The difference in β_T values presented in [6] for the saturation line at 200°C from the corresponding values calculated by Eq. (1) is less than 2%.

Cesium. The equation of state of liquid cesium in the form of Eq. (1), constructed from experimental PVT data of [1], has the coefficients A_{ij} presented in Table 7.

The mean-square error of the approximation is 7.5 bar, which corresponds to a deviation of calculated density values from experiment of not more than 0.1%.

The recommended range of application of the liquid cesium equation of state is 500-1000°K at pressure from P_s to 10^8 Pa (1000 bar). We have expanded the range of applicability of the proposed equation over pressure in comparison to the experimentally studied pressure range [1], just as in the case of rubidium, on the basis of good agreement of the low temperature cesium density values calculated by the proposed equation with analogous data from [8].

Table 8 shows smoothed density values of liquid cesium at various temperatures and pressures.

The values of pressure, isothermal compressibility, and thermal expansion for various molar volumes and temperatures calculated from Eq. (1) are presented in Table 9.

Figure 3 shows isothermal compressibility curves for T = 500, 750, and 1000°K and along the saturation line, together with a curve for β_T along the saturation line obtained in [9] by speed of sound measurements. The maximum deviation of the present β_T data from that of [9] comprises 7% (in [9] the authors' estimate of β_T uncertainty was 5.3%).

Thus, the analysis of error in experimental data performed in [1] together with analysis of the approximated polynomials for PVT curves and their derivatives indicate satisfactory reliability of the proposed equations of state for alkali metals in the liquid phase.

NOTATION

P, pressure; V, volume; T, temperature; A_{ij}, coefficients of the polynomial; β_T, isothermal compressibility; α_p, thermal expansion.

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