DENSITY OF FUSIBLE METALS PASSING THROUGH THE MELTING POINT

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The density and thermal expansion of the low-melting and, in particular, the alkali metals near the "melting-freezing" phase transition point have been studied many times [1]. However, in most cases the studies were made either of the solid or liquid phase only, and therefore the studies were of different specimens of the substances. If we also consider that the compositions of the specimens studied by different authors differed significantly and that the number of measurements in the immediate vicinity of the melting point is usually not sufficient to ensure high measurement accuracy of the temperature and other thermal relations, it is natural that there is still very little detailed information available on density changes during melting and freezing of the alkali metals and most of the other metals.

The present paper includes results of studies of pure rubidium and gallium density and also of a series of specimens of potassium, rubidium, and cesium with impurities in the vicinity of the melting point. The studies were made using a dilatometer with intermediate medium, similar to the pycnometer method for measuring the density of solid bodies [2].

This method has been used previously, e.g., in [3] to study the thermal expansion of liquid cesium, and is nearly the only method which permits carrying out equally accurate measurements for the liquid and solid phases of the same specimen.

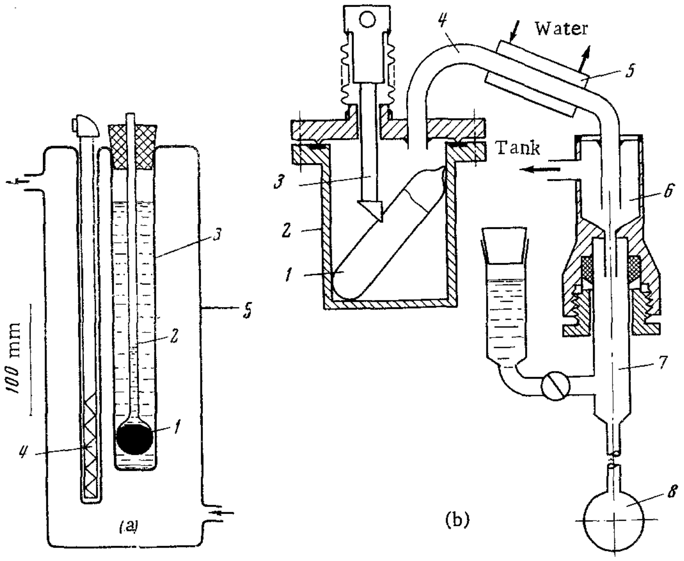

Fig. 1

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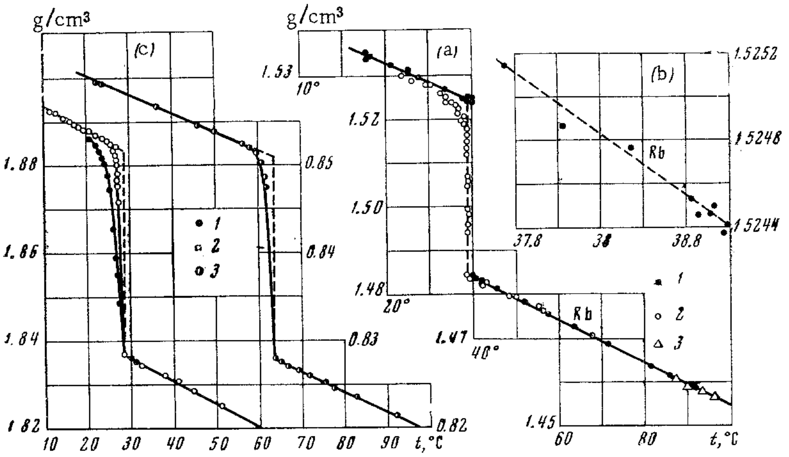

Fig. 2

TABLE 1. Composition of Alkali Metal Specimens, wt. %

Specimen	Mass, g	Na	K	Rb	Cs	Ca	Other
K	13.8	<1.1	98.5	0.1	0.1	0.1	0.2
Rb1*	19.7	0.003	0.009	99.93	0.001	0.001	0.005
Rb2†	14.6	0.1	9.0	>89	1.0	0.1	1.0
Cs1 ‡	28.4	<0.003	<0.018	<0.001	99?	<0.003	Oxides
Cs2**	24.3	0.05	0.5	1.0	98	0.1	0.5

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*Analysis of lot.

†RETU-118-59.

‡Oxidized during charging.

**RETU-117-59.

TABLE 2

Quantity	Rb1	Rb2	Cs1	Cs2	K	Ga
t' °C from	14.6	18	12.7	19	20.0	19.0
t'' °C to	91.6	66	50.8	32	91.9	79.3
t_* °C	39.16	38.6	28.5	28.2	63.3	29.80
Δt_*, deg	<0.05	>10	~3	~8	~3.5	<0.05
$\delta\rho_*$, %	2.625	—	2.48	—	2.7	—3,39
ρ_*', g/cm³	1.5244	—	1.883	—	0.851	5.895
ρ_*'', g/cm³	1.4844	—	1.837	—	0.828	6.095
b'	4.40	—	5.16	—	2.1	2.69
b'' g/cm³·deg	4.81	4.7	5.29	—	2.4	6.62

Note. Single prime relates to solid phase, double prime to liquid phase.

1. The majority of the experiments were conducted using the liquid dilatometer method with VM-1 degassed vacuum pump oil as the intermediate medium. A schematic of the apparatus, fabricated from molybdenum glass, is shown in Fig. 1a. The dilatometer reservoir 1 (20–25 cm³) was filled to about $\frac{4}{5}$ of its volume with the metal, and oil was poured above the metal in the reservoir into the expansion tube 2 (ϕ 4 mm) (under a vacuum). The dilatometer thus prepared was mounted in the VM-1 oil bath 3 of the thermostatting sleeve 5, which was heated with water from a U-10 thermostat. The temperature in the experiments was measured by the type TSPN-1 resistance thermometer 4 with $R_0 = 100\ \Omega$, and the liquid level variations in the expansion tube during changes of the specimen volume were measured by a type KM-6 cathetometer, using two scribe lines on the outer surface of the expansion tube as reference lines. When using readouts 5-7 relative to both reference lines, the error of the level measurements did not exceed ±0.01 mm.

The second rubidium specimen (Table 1 and Fig. 2) was studied in a gas dilatometer with helium as the intermediate medium, based on the principle of measuring the gas pressure changes above the metal

TABLE 3

	t	$\Delta\rho\cdot10^4$	t	$\Delta\rho\cdot10^4$	t	$\Delta\rho\cdot10^4$
Rb (1)	45.21	220.5	38.99	652.8	56.70	167.5
	24.22	722.5	38.67	658.7	58.02	161.2
	37.06	659.5	38.81	653.4	63.11	137.0
	38.55	665.6	38.88	652.7	15.03	752.0
	39.11	650.7	39.02	653.1	24.45	714.3
	41.28	244.2	39.14	652.2	70.96	98.8
	24.62	713.0	26.86	706.5	76.18	74.7
	40.12	247.1	39.18	251.6	81.20	49.5
	51.25	195.0	37.61	656.8	85.94	27.3
	39.77	248.0	38.24	655.7	91.58	1.0
	39.17	252.7	39.14	657.2	20.28	734.0
	39.46	250.4	39.24	251.0	15.52	755.3
	39.12	651.9	32.74	678.8	14.60	761.5
Cs (1)	30.2	—6.3	26.5	435.6	27.6	1.6
	20.0	513.6	17.0	527.3	15.8	536.4
	19.0	518.8	30.8	—10.3	24.7	465.4
	19.2	516.1	24.0	490.4	24.8	465,7
	26.8	398.6	23.0	497.0	23.2	495.5
	17.6	526.2	44.4	—84.2	25.6	466.6
	27.8	390.6	40.6	—63.6	26.0	451.6
	19.1	516.9	50.3	—114.9	26.7	405.6
	18.4	520.3	32.0	—17.6	27.0	348.6
	25.9	465.6	50.8	—117.1	18.4	520.6
	24.5	489.3	36.7	—41.3	24.6	486.2
	24.8	487.1	28.7	—1.1	26.6	413.6
	25.0	483.9	28.3	355.6	26.4	433,6
	25.9	458.6	16.5	533.1	13.4	550.0
	29.4	—4.4	27.9	0.6	12,7	551.6

	t	$\Delta\rho\cdot10^4$	t	$\Delta\rho\cdot10^4$	t	$\Delta\rho\cdot10^4$
K	71.5	—18.3	46.4	268.4	62.2	201.1
	77.7	—33.3	56.4	246.9	23.0	318.2
	65.8	—5.1	22.4	318.4	61.2	224.1
	63.3	1.1	75.5	—27.2	60.3	244.1
	22.7	318.0	82.4	—48.5	57.4	245.6
	59.6	238.1	91.9	—113.7	20.0	324.1
	49.9	261.3	69.0	—12.5	61.0	226.1
	35.8	291.0	62.7	196.1		
Ga	55.87	—180	46.28	—110	29.66	—2004
	19.61	72	31.97	—15	29.71	—2004
	27.57	17	25.52	25	29.75	—2005
	44.36	—97	21.82	56	22.19	—1979
	62.89	—221	15.78	90	21.17	—1972
	71.92	—260	19.56	—1970	39.72	—66
	50.38	—145	23.84	—1983	48.19	—119
	18.58	77	28.87	—1995		
	79.27	—307	29.44	—1997		

specimen, using a differential manometer located in the same thermostat together with the compensating reservoir.

2. The dilatometer basic volume was calibrated in the same apparatus using twice-distilled water. Scales of the ADV-200 type were used for weighing. The water density in the volume calculations was taken from [4]; the glass linear expansion coefficient was taken from [5]. Calibrations were also made of the dilatometers and expansion tubes using oil over the entire operating temperature range, with a special measurement being made of the temperature dependence of the VM-1 oil present in the dilatometer and calibrated capillary. In the calibrations it was found that the additional error from the oil film remaining on the tube walls does not exceed 0.001% with conventional cleaning of the glass surface. The maximal dilatometer volume measurement error did not exceed ±0.01%. In the dilatometers used the dependence of the liquid column height on the volume was practically linear, and the rms deviation of the calibration points from the interpolating straight line was no more than 0.005%.

3. The dilatometers were filled with the metals (potassium and the first rubidium and cesium specimens) through the expansion tube by vacuum distillation. A schematic of the setup is shown in Fig. 1b. The additional unit 7, which connected the dilatometer with the distillator, was soldered to the expansion tube for the filling operation. The glass ampoule 1 with the metal was placed in the boiler 2, and after a vacuum of $\sim10^{-5}$ torr was reached in the entire system, the ampoule was broken by the hammer 3. The metal vapors exited through the tube 4 and condensed near the cooler 5. The liquid metal drained through the intermediate volume 6 into the dilatometer 8. The intermediate volume and the dilatometer were also heated. Immediately after termination of distillation, the vacuum oil was poured into the dilatometer from the vessel 7. During the filling process the metal could come into contact only with stainless steel and glass.

The second rubidium and cesium specimens, and also the gallium specimen, were fed into the dilatometer through a stainless steel capillary from the intermediate crucible, where the metal was covered with an oil layer.

4. The dilatometric experiment preparation technique prevented reliable measurement of the alkali metal specimen mass; therefore, in the experiments we investigated only the relative changes of the specimen volume, and in the density calculations it was necessary to use a reference density value for some temperature.

A glass capillary (diam. 1 mm) pycnometer was used to measure the liquid rubidium (purity 99.98%, similar to specimen 1) reference density. The measurements were made using the same apparatus. The pycnometer was calibrated with mercury prior to the experiment. In the calculations the mercury density was taken from [4]. The pycnometer was also filled through the capillary by distillation. After filling, the pycnometer was also sealed off from the filling system (under vacuum) in the upper part of the capillary. The metal mass was determined after measuring the filling temperature, using the technique described in

[1], i.e., after removing the metal from the fractured pycnometer. The mass of the small glass fragments which appeared after breaking off the capillary did not exceed 10 mg for a metal mass of 12.8 g.

The results of the pycnometric experiment were presented previously in [8] and are reproduced in Fig. 2a.

All the measurements were made only under steady-state temperature conditions, both when increasing temperature from point to point and when reducing temperature with repeated passage through the melting-crystallization region. The thermostat maintained the temperature with oscillations of ±0.02 deg. The measurements of the temperature and level of the liquid in the expansion tube were initiated only after stabilization of the level, which required 3-5 h in the melting region. The repeatability of the measurement results in both the basic and calibration experiments was no worse than 0.005%. For the indicated dilatometer dimensions the instrumentation provided reliable recordings of density changes of the alkali metal specimens of $5 \cdot 10^{-5}$ g/cm^3 and $5 \cdot 10^{-4}$ g/cm^3 for the gallium specimen.

5. Table 1 presents data on the initial composition of the alkali metal specimens and also the masses of the specimens. The system construction and filling technique make it possible to assume that there was no marked variation of the elemental and quantitative composition of the specimens during the charging process. The absence of any systematic scatter of the measurement results apparently indicates that there were no marked composition changes in the course of the experiments either. The tested gallium specimen (55.516 g) contained 0.01% impurities, primarily aluminum.

Table 2 and the curves of Fig. 2 present the basic experimental results. The following reference points for the liquid metal density were used in calculating the quantities indicated in the table and shown graphically:

a) for Rb from pycnometric experiment

$$\rho_0 = 1.4592\ (\pm\ 0.0006)\,\mathrm{g/cm^3}\ \text{at}\ \ 91.5^\circ\,\mathrm{C}$$

b) for Cs from calculation using the equation of [6]

$$\rho_0 = 1.837\ (\pm\ 0.005)\,\mathrm{g/cm^3}\ \text{at}\ \ 28.5^\circ\,\mathrm{C}$$

c) for K from [7]

$$\rho_0 = 0.828\ (\pm\ 0.005)\,\mathrm{g/cm^3}\ \text{at}\ \ 63.5^\circ\,\mathrm{C}$$

d) for Ga from [8]

$$\rho_0 = 6.095\ (\pm\ 0.003)\,\mathrm{g/cm^3}\ \text{at}\ \ 29.8^\circ\,\mathrm{C}$$

The curves in Fig. 2 show that for the contaminated specimens (which can also be classified as alloys) the ingot volume changes upon approach to the melting temperature so that the variation of its average density is quite nonlinear, i.e., there exists a premelting zone which expands with reduction of specimen purity. Beyond the limits of the premelting zone in the solid state temperature range investigated, the temperature dependences of the density are linear to within 0.01%. The premelting zone is not detected for the high-purity rubidium and gallium specimens up to temperatures 0.05 deg below the melting point. This can be seen quite clearly from the large-scale plot for rubidium shown in the upper right corner of Fig. 2b.

On the liquid phase side no anomalies were observed for any of the specimens studied down to temperatures 0.05 deg above the temperature for initiation of solidification, and the temperature dependences are linear to within 0.01% in the ranges studied. Nor were any anomalies found in the temperature-density dependence of liquid gallium, which was supercooled by 14 deg, although the temperature coefficients of the solid and liquid phase densities in this temperature region are significantly different. The other metals did not supercool spontaneously under the experimental conditions.

The uncertainty in the composition of the Rb2, K, Cs1, Cs2 specimens, and also the uncertainty in the nature of the impurity influence on the magnitude of the density, make it impossible to define the reference value sufficiently reliably. Therefore, the density of the Rb and Cs specimens of different composition was assumed to be approximately the same at the temperature for initiation of solidification. The curves of Fig. 2 for the Rb2 and Cs2 specimens are purely illustrative, showing the relative change of the solid phase density for metals of different composition. The numerical results of the experiments do not exceed the possible error limits of the studies noted in the list of references and other investigations; however, the data of other authors are not presented because of the large discrepancies in the experimental conditions.

Table 2 shows the quantities which can be determined independently in the experiments:

a) solidification initiation point t_* °C, essentially equal to the melting point for pure Rb and Ga;

b) magnitude of premelting zone Δt_*^- °C;

c) magnitude of density jump at the melting point relative to the solid phase density $\delta\rho_*$% (for the specimens with impurities the solid phase density at t_* was calculated using the temperature coefficient calculated for the region beyond the premelting zone);

d) density temperature coefficients b, g/cm^3·deg for the solid and liquid phases;

e) also shown are the calculated values of the density in g/cm^3 at t_* for the solid and liquid phases, which can be used for practical purposes.

The additional measurement error (in relation to the error of the reference density values) at the end of the studied temperature interval does not exceed ±0.05% for rubidium, cesium, and gallium and ±0.2% for potassium. The temperature measurement error in the experiments did not exceed ±0.03 deg. However, t_* was determined with an error of no more than 0.05 deg only for pure Rb and Ga, since the volume jump was very abrupt. For the specimens having a premelting zone, t_* is determined with an error of 0.1-0.2 deg. The probable error of the determination of the density temperature coefficients b does not exceed ±3%.

The experimental results are presented in Table 3, where

$$\Delta\rho = \rho_t - \rho_0 \quad [\mathrm{g/cm^2}]$$

Let us examine the influence of vacancies on the density temperature dependences. In the case of significant increase of the vacancy concentration, the solid phase density near the melting point should decrease more rapidly than shown by the linear law. However, in the experiments with pure Rb and Ga this phenomenon was not observed, and the premelting effect appears to exist only for the metals with impurities (alloys) and is explained by the nonhomogeneity of the specimen in the premelting zone. Nor were any deviations of more than 0.05% from the linear relations observed in the study of the temperature dependences of the electrical resistance of pure Rb and Ga [9]. All this indicates either that the vacancy concentration is very small for these metals or that vacancy formation does not lead to any significant change of the density and electrical conductivity, as was suggested in [10], or finally that the solid state temperature intervals studied are not sufficiently large to identify the vacancy influence effect.

LITERATURE CITED

1. K. A. Yakimovich and S. Ya. Saars, "Measurement of liquid Rb density near the melting point," Teplofizika vysokikh temperatur, vol. 5, no. 3, 1967.
2. S. Sh. Kivilis, Technique for Measuring Density of Liquid and Solid Bodies [in Russian], Standartgiz, Moscow, 1959.
3. M. Eckardt and E. Graefe, "Zur Kenntnis des physikalichen Verhaltens des Cäsiums," Z. Anorg. Chem., vol. 23, p. 378, 1900.
4. Thermophysical Properties of Substances [in Russian], Gosenergoizdat, Moscow-Leningrad, 1956.
5. Handbook on Glass Production [in Russian], vol. 1, Gosstroiizdat, Moscow, 1963.
6. É. É. Shpil'rain, Yu. A. Soldatenko, K. A. Yakimovich, et al., "Experimental study of thermophysical and electrophysical properties of alkali metals at high temperatures," Teplofizika vysokikh temperatur, vol. 3, no. 6, 1965.
7. E. I. Gol'tsova, "Density of lithium, sodium, and potassium up to 1500-1600°C," Teplofizika vysokikh temperatur, vol. 4, no. 3, 1966.
8. A. S. Basin and A. N. Solov'ev, "Study of liquid metal density by the gamma method," collection: Studies of Thermophysical Properties of Substances [in Russian], Nauka, Novosibirsk, 1967.
9. B. E. Semyachkin and A. N. Solov'ev, "Experimental study of electrical resistance of alkali metals," collection: Studies of Thermophysical Properties of Substances [in Russian], Nauka, Novosibirsk, 1967.

10. Ya. A. Kraftmakher, "Thermal capacity of metals at high temperatures. Formation of vacancies and phase transitions of the second kind," collection: Studies in Solid State Physics [in Russian], Nauka, Novosibirsk, no. 1, 1967.