DENSITY OF MELTS OF ALKALI METALS AND THEIR Na-K-Cs AND Na-K-Rb TERNARY SYSTEMS

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ABSTRACT

In this paper the results of the experimental study of the density of liquid alkali metals and alloys of the Na-Cs-K and Na-K-Rb ternary systems are presented. Also presented is the improved vacuum two-capillary pycnometer for the study of density of liquid alkali metals. Density polytherms of alkali metals and their binary and ternary alloys up to 700 K are described well by linear equations with negative temperature coefficients (TC). Density isotherms of ternary alloys at constant X_{Na}:X_{Cs} ratio reveal a small positive (at X_{Na}:X_{Cs}>1) or negative (at X_{Na}:X_{Cs}<1) divergence from the additivity principle. X_{Na} and X_{Cs} are concentrations of Na and Cs in at.%, respectively. Curves of equal values of density are also given for the whole composition triangle at 373 K.

INTRODUCTION

Alkali metals and alloys have a unique combination of physicochemical properties, such as extremely high electrical and thermal conductivities, small densities and viscosities, low melting temperatures and work functions, wide temperature ranges of a liquid state, large heat of evaporation, etc. Therefore, they are widely used in modern science and technology, for example, in nuclear energetics, emission electronics, new power-intensive chemical current sources, medicine, and other fields [1-4].

In this work we present the experimental data on the density of liquid alkali metals and the Na-K-Cs and Na-K-Rb ternary systems.

Analysis of the available literature on the subject reveals there are many works devoted to the study of the physicochemical properties of alkali metals and their alloys [5,7-9]. However, the experimental data of various authors on some properties is distinctly different; only the densities of four ternary Na-K-Cs alloys have been found in the literature, including two with compositions close to the eutectic [5,8,9].

TECHNIQUE AND DEVICE FOR THE MEASUREMENT OF THE DENSITY OF LIQUID ALKALI METALS

The most precise method to study the density of liquid metals is the pycnometer technique. A principal shortcoming of the latter is the process of filling the pycnometer with studied liquids through thin capillaries. It involves a large probability of forming breaks in the pillar of liquid in the capillaries and small gas cavities in the bulk of the melt and near the walls of the capillary. This deficiency of the method, amplified by a small density and high

saturated vapor pressure of alkali metals, may considerably decrease its reliability and precision.

In the present work we used a completely soldered two-capillary vacuum pycnometer (Fig.1), which enables to overcome the indicated problems and obtain reliable data on the density of liquid alkali metals. The relative error for the density is 0.1% with 95% reliability.

The pycnometer was made from glass. Inside the loading bunker 1 there is a glass container 2, separated by a hemispherical partition 4 from an ampule 3 with the initial metal, and a hammer 5 in the shape of a metallic pivot covered with glass. Bunker 1 is soldered to the chamber 6 perpendicularly to its body. Chambers 6 and 7 are joined by tube 8. Two metered capillary tubes 9, with marks 10 and 11 for determining the level of the liquid in capillaries, are soldered to its lower ends. Chamber 12 is soldered to the lower ends of capillaries 9. It should be noted that the right capillary is soldered to the lower edge of chamber 12 at its bottom, which enables delivery of the studied liquid into the metered chamber in a "from the bottom upwards" regime. The latter prevents liquid spattering and formation of cavities. The pycnometer was joined above the A-A level to the ultrahigh vacuum pump with chambers 6 and 7 oriented vertically (chamber 7 located lower than chamber 6).

After thermo-vacuum treatment of the pycnometer for several hours, the partition 4 is destroyed with the hummer 5, and the liquid metal fills chamber 6, spreading and forming a wide and open surface. Further degassing of the liquid metal is continued, providing a removal of possible gaseous inclusions. An advantage of this device compared to the other well-known techniques is the effectiveness of the thermo-vacuum treatment. One can note that the lower end of the ampule in the capillary 13 prevents the device and the metered chamber from delivering the contaminated surface layer of the researched liquid. When the thermo-vacuum treatment is finished, bunker 1 is soldered off from balloon 6 along the B-B level, and the pycnometer is disconnected from the vacuum pump along the A-A narrowing. Then, by slowly rotating the device to its working vertical position, chamber 12 is filled by a laminar flow of the liquid metal from chamber 6 through the right capillary. The entire device is located inside an air thermostat, which allows orientation of the pycnometer in any position. Simplicity and reliability of this method and high productivity of the pycnometer technique permit to study the temperature dependency of the density in detail. The data on the density of the Na-K-Cs alloys from [5] (curve 5) and our data (curve 6) are shown in Fig.3. In the temperature range of 100^0C we obtained 40 experimental data points, including 20 data points at increasing, and 20 at decreasing temperature. Only 3 data points at increasing temperature were obtained in [5] by the traditional two-capillary method.

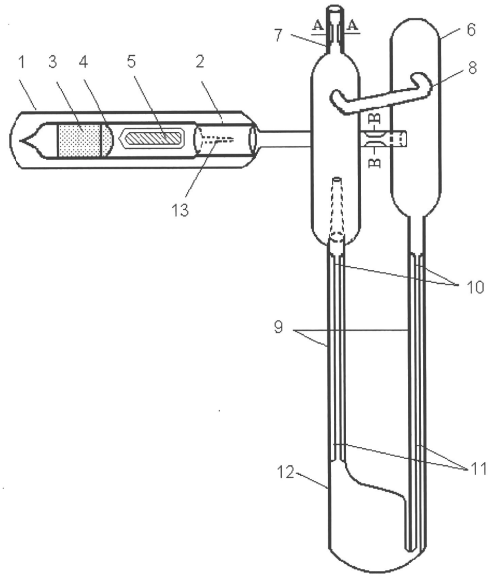

Fig.1. Two-capillary vacuum pycnometer for measuring the density of liquid alkali metals.

RESULTS OF DENSITY MEASUREMENTS FOR ALKALI METALS AND ALLOYS OF THE Na-K-Cs AND Na-K-Rb SYSTEMS

Phase diagrams of the binary systems of alkali metals are given in the references. For single Na-K-Cs system the phase diagram was found only in [7]. It reveals a ternary eutectic alloy with content of 13.9 at.% of Na + 43.5 at.% of K + 42.6 at.% of Cs at the lowest melting point of 195 K for metallic alloys. No phase diagram for the Na-K-Rb system is available, although one can expect that this system also has a ternary eutectic alloy. The ternary Na-Cs-K alloys were prepared by adding K to Na-Cs binary alloys at constant X_{Na}:X_{Cs} ratio. The metals of high purity were used: Na, K and Cs with 99.999%, and Rb with 99.996% content of the base element.

The ternary Na-K-Rb alloys were prepared by adding Rb to Na-K binary alloys at constant X_{Na}:X_K ratio. The sections and compositions of the ternary alloys and the composition triangle are presented in Fig.2. We studied 110 Na-Cs-K alloys along ten sections and 40 Na-K-Rb alloys along four sections. The densities of 38 alloys of the first system and 18 alloys of the second system have been measured. The density of liquid metals and their binary alloys are well-studied [5]. Temperature dependence of their density D(T) over a wide range of temperatures (up to about 700 K) is described by linear equations with negative temperature coefficient:

$$D(T)=D_1-b(T-T_1), \qquad (1)$$

where T_1 is the melting temperature, D_1 is the density at T_1, and b is the temperature coefficient of density. The values of T_1, D_1 and b for pure alkali metals and their binary eutectic alloys are given in Table 1.

Table 1. Temperature dependence of density of liquid alkali metals and their eutectic alloys

Me	**Li**	**Na**	**K**	**Rb**	**Cs**
T_1, K	453.6	371.0	336.8	312.6	301.5
D_1, kg/m^3	525.5	961.1	850.4	1524.8	1885.1
b, kg/m^3·K	0.009	0.243	0.235	0.462	0.511
Me_1-Me_2 eutectic	**Na-K**	**Na-Rb**	**Na-Cs**	**K-Rb**[*)]	**K-Cs**
X_2, at.%	68.1	82.1	21	~70	50
T_1, K	260.5	268.6	241.3	307.4	235.1
D_1, kg/m^3	876.6	1186.6	1764.5	1523.4	1507.6
b, kg/m^3·K	0.233	0.308	0.560	0.362	0.346

*) K-Rb binary alloy has the minimum melting temperature.

In the literature we found only the values of density for four Na-K-Cs ternary alloys, including one with 11.8 at.% of Na + 47.4 at.% of K + 40.8 at.% of Cs composition close to the eutectic alloy [8].

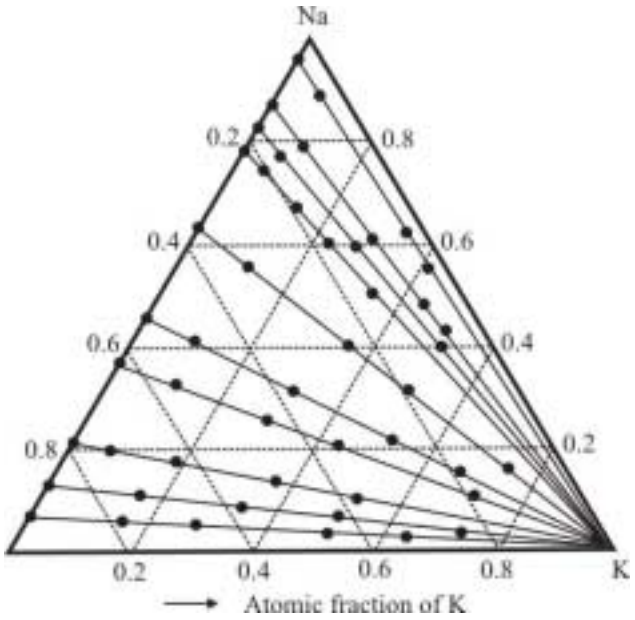

Fig.2. Compositions of 38 ternary alloys of the Na-K-Cs system along the sections, for which the density is measured.

The temperature dependence of the density of ternary alloys of the researched systems is described by linear equations of type (1). Polytherms of density for some ternary alloys of the Na-Cs-K system are presented in Fig.3. As it is evident from Fig.3, reproducibility of the results is sufficiently high.

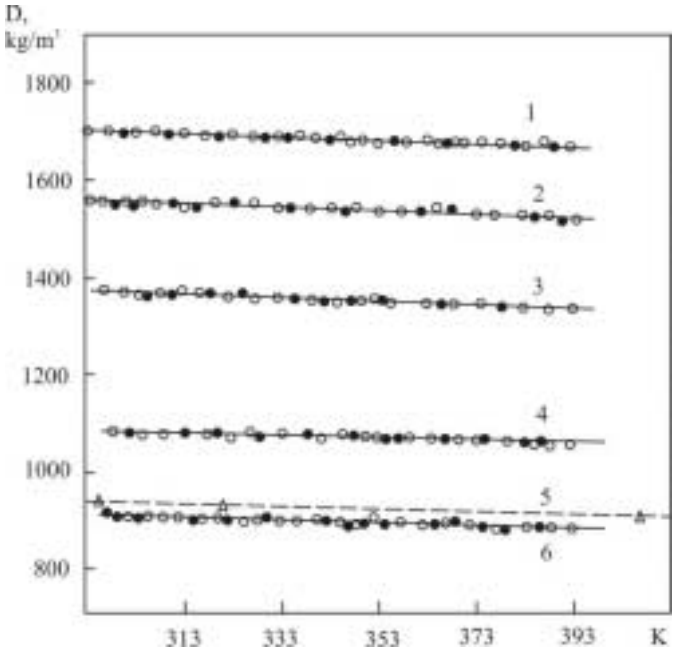

Fig.3. Temperature dependence of density of the ternary alloys of the Na-K-Cs system:
1 – Na+12.5 K+68.0 Cs; 2 – Na+34.7 K+56.6 Cs; 3 – Na+66.3 K+31.0 Cs;
4 – Na+38.3 K+9.1 Cs; 5 – Na+42.1 K+1.7 Cs; 6 – Na+40.5 K+1.0 Cs by at. %.

Density polytherms of the alloy with the composition of 13.3 at. % of Na+40.4 at. % of K+46.3 at. % of Cs close to the eutectic are given by equation:

$$D(T)=1493-0.492\ (T-T_e),\quad kg/m^3, \tag{2}$$

where T_e is the eutectic temperature. In recent work [9] the density of the eutectic alloy of the Na-K-Cs system was carefully studied. It was found, that the temperature dependence of the density over the range of temperatures from 293 to 1101 K is expressed by equation:

$$D(T)=1562.76-399.63\cdot10^{-3}\ T-19.15\cdot10^{-6}T^2\ ,\ kg/m^3. \tag{3}$$

The density values calculated using equations (2) and (3) are in a satisfactory agreement with our results within the comparable temperature intervals.

Density isotherms of the ternary alloys at 293, 333 and 373 K were plotted for all studied sections. It is concluded that isotherms built along sections beginning with Na-Cs binary alloys reveal either negative (at $X_{Na}>X_{Cs}$) or positive (at $X_{Na}<X_{Cs}$) deviation from the additive curve. Within the area of the concentration triangle of the Na-Cs-K system the curves of equal densities (isolines) at 373 K were plotted (Fig.4). It may be pointed out that the ternary alloys, corresponding to isolines 8 and 9, have density values of 1000 kg/m^3 and 900 kg/m^3, equal to the density values of water and petroleum, respectively

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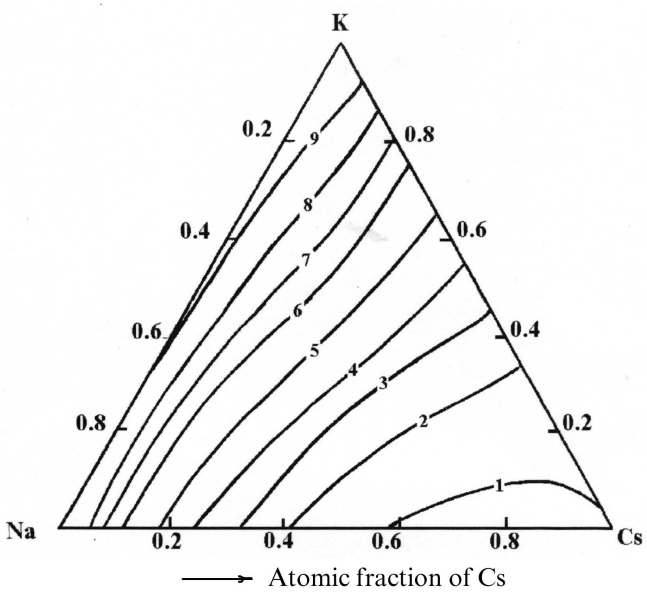

Fig.4. Curves 1 through 9 are compositions of the Na-Cs-K ternary alloys, having the equal values of density at 373 K: 1 – 1700; 2 – 1600; 3 – 1500; 4 – 1400; 5 – 1300; 6 – 1200; 7 – 1100; 8 – 1000; 9 – 900 kg/m^3. The densities of Cs, Na and K are equal to 1794, 927 and 818.3 kg/m^3, respectively.

For the Na-K-Rb system the alloys along four sections have been studied, adding Rb to Na-K binary alloys at $X_{Na}:X_K$ = const. The results for this system are similar to those for the Na-Cs-K system. All density polytherms are described by linear equations with negative temperature coefficients, and density isotherms reveal a negative divergence from the additive curves.

CONCLUSION

For the first time the temperature and concentration dependencies of the density of 38 ternary alloys of the Na-Cs-K system and 18 alloys of the Na-K-Rb system have been obtained. It was concluded that the density polytherms over the range of temperatures from 290 to 700 K are described by the linear equations with negative temperature coefficients. The isotherms of density reveal either positive or negative divergencies from the additive curves, depending on the composition of the initial Na-Cs binary alloys. The density isotherms of the Na-K-Rb ternary alloys reveal a negative divergence from the additive curves only.

The isolines of density at 373 K were plotted for the Na-Cs-K system over the area of the concentration triangle.

It is necessary to note that a study of the physicochemical properties of alkali metals and their alloys is very difficult due to their high chemical activity and large saturated vapor

pressure. It requires elaboration of new methods, devices and techniques that take into account the peculiarities of handling and working with alkali metals.

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