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The Densities and Molal Volumes of Molten Mixtures of Potassium Chloride and Barium Chloride

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This paper reports the results of measurements of the densities of molten mixtures of potassium chloride and barium chloride. Values for the densities and molal volumes at 800° for each composition have been obtained by interpolation of the plotted data. Similarly, the temperature coefficients of the densities have been evaluated from these plots. The paper describes the apparatus and techniques employed with special reference to an improvement in the sinker method of density determination whereby errors due to condensation of salt vapors on the suspension wire may be eliminated.

Introduction

Values of the densities of molten salt mixtures are important for the calculation of other properties of these melts as well as in certain technological applications. For example, in magnesium alloy founding operations saline fluxes are employed whose compositions are within the system potassium chloride–magnesium chloride–barium chloride. As a beginning to the investigation of this ternary system, we have studied the binary system potassium chloride–barium chloride, to obtain data on densities and on surface tensions of the melts. The density measurements are reported in the present paper and the surface tension measurements in the following paper.

Various investigators have reported determinations of the densities of molten salt mixtures. For example, Mashovetz and Lundina[2] published data on mixtures of potassium chloride and barium chloride, the system with which this paper is concerned. The work has been repeated, partially because Mashovetz and Lundina reported isotherms for only two temperatures, and particularly because they showed density values for only two mixtures in addition to values for the pure components. Their work covered other systems as well, such as the sodium chloride–potassium chloride, sodium chloride–magnesium chloride and potassium chloride–magnesium chloride systems.

The means available for precise measurements of density in molten salt mixtures are limited to the dilatometric method and to the buoyancy or "sinker" method, the former being applicable only at temperatures below about 750° due to the vigor with which molten salts attack the silica dilatometers at higher temperatures. Boardman and coworkers[3] who worked with this type of apparatus claimed a higher order of accuracy for the former method than could be obtained using the sinker method. The basis of their claim was the error due to condensation of salt vapors on the wire from which a sinker is suspended which results in the measured values being too low. The 750° temperature limitation of the dilatometer method precludes its use on many systems which have considerable theoretical and technical interest, because such systems require higher temperatures in order for the mixtures to be in the molten state. Jaeger[4] described the apparatus based upon the sinker method which he used for making measurements on molten salts at temperatures as high as 1600°. He mentioned the error caused by condensation of volatile salts upon the wire supporting the sinker. In the present investigation a simple and reliable means was devised for preventing this source of error and is described below as part of the apparatus employed.

Experimental

Preparation of Salt Mixtures.—The potassium chloride used in this investigation was Baker and Adamson reagent grade material and was used without further purification other than to heat it in a muffle furnace for 10 hours at 600° to remove traces of water.

In order to obtain anhydrous barium chloride, reagent grade dihydrate obtained from Merck and Company was first heated for 24 hours in a six-inch porcelain casserole on a hot plate at maximum power input to remove most of the water and was then heated for 10 hours at 800° in a muffle furnace to complete the dehydration.

The salt mixtures below forty mole per cent. barium chloride were made up in quantity and stored prior to use. Those of higher barium chloride content were made up at the beginning of each experiment.

Analysis of Melt Compositions.—Analyses were made on the melts following completion of the measurements by dissolving the melts from the crucibles and determining the barium content by weighing as the carbonate. Attempts to determine barium as the sulfate were not successful due to the error caused by adsorbed potassium sulfate which could not be washed out completely.

Description of Apparatus.—Most of the features of the apparatus will be obvious from Fig. 1 and its accompanying legend. The unique features in apparatus design and in technique are (a) the means of preventing condensation of salt vapors upon the suspension wire and (b) the technique for accurate location of the surface of the melt making possible an accurately reproducible depth of immersion of the sinker.

Prevention of condensation of salt vapors was achieved by the use of a stream of air introduced through the side tube (22) of the vertical silica anti-condensation tube (23). The latter tube (4 mm. inside diameter and 44 cm. long) was suspended and pivoted for accurate alignment as shown in the insert of Fig. 1. The flow of air required did not interfere with the free movement of the wire and produced no drag upon it or any resultant interference with the accurate use of the balance. The freedom of the furnace to be raised and lowered and to be swung to one side was necessary in order that the anticondensation tube might be used. Furthermore, this movement of the furnace made possible periodic determination of the apparent mass of the sinker and the accurate location of the level of the melt in the crucible. The temperature was not measured inside the melt because

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[1] Taken from a portion of a thesis submitted by Marvin R. Bothwell to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] V. P. Mashovetz and Z. F. Lundina, "Ukrain. Akad., Nauk Inst. Khim. Sbornik Trudov Pervoi Vsesoyuznoi Kontferenzii Novodnium Rastvoram" (Proc. 1st All-Union Conf. Non-aqueous Solutions), 1935, pp. 191–212.

[3] N. K. Boardman, F. H. Dorman and M. J. Heymann, *J. Phys. Colloid Chem.*, **53**, 375 (1949).

[4] F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 278–307

TABLE I

DENSITIES OF $KCl-BaCl_2$ MIXTURES[a] (IN GRAMS PER MILLILITER)

0% $BaCl_2$		8.4% $BaCl_2$		13.1% $BaCl_2$		24.4% $BaCl_2$		29.8% $BaCl_2$		33.3% $BaCl_2$	
T	*d*	*T*	*d*	*T*	*d*	*T*	*d*	*T*	*d*	*T*	*d*
792	1.506	793	1.692	790	1.771	790	2.056	802	2.125	796	2.226
793	1.506	814	1.679	810	1.760	812	2.041	820	2.110	815	2.201
803	1.501	826	1.677	830	1.746	830	2.031	836	2.098	826	2.187
810	1.492	830	1.669	848	1.737	850	2.016	844	2.093	827	2.166
816	1.492	837	1.663	864	1.737	869	2.006	866	2.078	840	2.156
823	1.487	840	1.662	888	1.723	888	1.996	869	2.077	850	2.147
829	1.482	840	1.662					879	2.071	870	2.134
830	1.483	840	1.662					884	2.067	881	2.127
841	1.476	853	1.646					901	2.056	891	2.120
841	1.477	857	1.647								
847	1.472	864	1.639								
852	1.469	878	1.639								
868	1.460	895	1.617								
869	1.457										
888	1.447										
896	1.444										

33.6% $BaCl_2$		45.7% $BaCl_2$		49.5% $BaCl_2$		63.3% $BaCl_2$		79.1% $BaCl_2$		100% $BaCl_2$	
T	*d*	*T*	*d*	*T*	*d*	*T*	*d*	*T*	*d*	*T*	*d*
789	2.226	791	2.426	781	2.493	825	2.731	884	2.926	969	3.141
802	2.215	806	2.414	799	2.480	839	2.724	895	2.915	983	3.131
818	2.204	813	2.409	818	2.467	852	2.715	910	2.904	994	3.125
818	2.210	824	2.401	832	2.457	861	2.710	924	2.895	1005	3.116
834	2.199	839	2.391	837	2.453	874	2.701	937	2.887	1013	3.111
838	2.185	850	2.383	847	2.447	892	2.687				
848	2.179	855	2.377	865	2.439	914	2.675				
859	2.173	872	2.364	885	2.427						
864	2.174	884	2.354								
876	2.167										
889	2.158										

[a] All compositions expressed in mole per cent.

of the interference with the vibration of the sinker which a submerged thermocouple would cause. The measuring thermocouple was introduced through the furnace support and was held almost in contact with the bottom of the crucible containing the melt. The readings of this thermocouple were carefully calibrated against those of a Pt *vs.* Pt–Rh thermocouple immersed in melts at temperatures covering the range employed in this investigation.

Procedure.—The experimental procedure followed the obvious steps of determining the apparent mass of the sinker and the submerged portion of the wire, first in water of known temperature and then in the salt mixture being investigated.

The reproducibility of the submersion of the sinker and suspension wire was guaranteed by the following technique. The balance was adjusted to equilibrium and the beam then freed for movement. The furnace holding either the melt to be investigated or a container of water at known temperature was raised slowly and carefully as the sinker and the surface of the liquid approached each other. At the instant of contact the sinker would momentarily be raised and would then be dragged under by the forces of adhesion and surface tension. The raising of the furnace was stopped at this point and a split spacer ring ($^{11}/_{16}$ inch high—not shown) was placed on top of the guide tube (30). The locking ring (28) was then fastened securely against the spacer ring and the latter then removed so that the furnace on being raised would be stopped by the locking ring (28). Thus a constant depth of immersion and hence a constant length of submerged suspension wire was obtained in every case.

When making measurements on salt melts the furnace and contents were permitted to come to thermal equilibrium before taking readings. Weighings were made with the balance beam free and in the rest position in order to eliminate errors due to damping of the balance beam vibrations by the melt. Three readings were made for a single determination of melt surface-level: one at the temperature at which the surface was located, one 10–20° below that temperature, and one 10–20° above the original temperature. Taking readings in this manner reduced significantly the time-consuming operations required in relocating the melt surface. We estimated that over this range of temperatures the change in level due to thermal expansion would be below the limit of accuracy of its location.

Experimental Results

In Table I the experimentally determined density values at various temperatures will be found arranged according to melt composition. These data have been plotted, and from the resulting smoothed curves values for the density at 800° were obtained by interpolation. These densities and their temperature coefficients are presented in Table II. Also in Table II are listed molal volumes calculated on the basis of the number of moles of the pure components.

In Table III are compared the values reported in the literature for density of potassium chloride at 800° and for its temperature coefficient with the values obtained in the present investigation. There are few data with which to compare our values obtained for the salt mixtures, but there are some published values for the density of pure barium chloride. Arndt and Gessler found a value of 3.12 g. per milliliter at 1000°, while Mashovetz and Lundina give the following expression, $d^t_4 = 3.032 - 0.00069(t - 1000°)$. Our value agrees well in magnitude with that of Arndt and Gessler but not too well with the value at 1000° of Mashovetz and Lun-

TABLE II

DENSITIES AND MOLAL VOLUMES OF KCl–BaCl$_2$ MIXTURES AT 800° AND TEMPERATURE COEFFICIENTS OF DENSITY

$$d^t{}_4 = d^{800°} - k(t - 800°)$$

BaCl$_2$, mole %	$d^{800°}$ (g./ml.)	$k \times 10^3$ (g./ml., °C.)	Molal vol. at 800° (cc./mole)
0.0	1.500	0.58	49.71
8.4	1.687	.64	50.86
13.1	1.765	.59	52.18
24.4	2.050	.63	52.29
29.8	2.123	.67	53.89
33.3	2.184	.70	54.49
33.6	2.217	.68	53.90
45.7	2.419	.77	56.10
49.5	2.480	.71	57.18
63.3	2.748	.65	57.93
79.1	2.912[a]	.68	60.54[a]
100.0	3.120[a]	.69	63.92[a]

[a] Extrapolated values.

dina. Our value for the temperature coefficient of the density, however, agrees well with that of the latter authors.

TABLE III

DENSITY OF MOLTEN POTASSIUM CHLORIDE

Density at 800°, g./ml.	Temp. coefficient $\times 10^6$, g./ml., °C.	Method of measurement	Investigator
1.507	−57	Balance	Brunner[5]
1.498	−54	Balance	Arndt and Gessler[6]
1.509	−59.5	Balance	Jaeger and Kahn[7]
1.499	−57	Balance	Mashovetz and Lundina[2]
1.517	−56	Dilatometer	Klemm[8]
1.502	−58	Balance	Results of present invest.

The probable error in our density measurements on the pure salts is estimated at less than ±0.2% and on the solutions at less than ±0.3%. This order of accuracy serves adequately for use in our measurements of the surface tensions of these salts to be reported in the following paper. It is not, however, considered of sufficient order to permit dependable calculations of values of the partial molal volumes for components of the solutions.

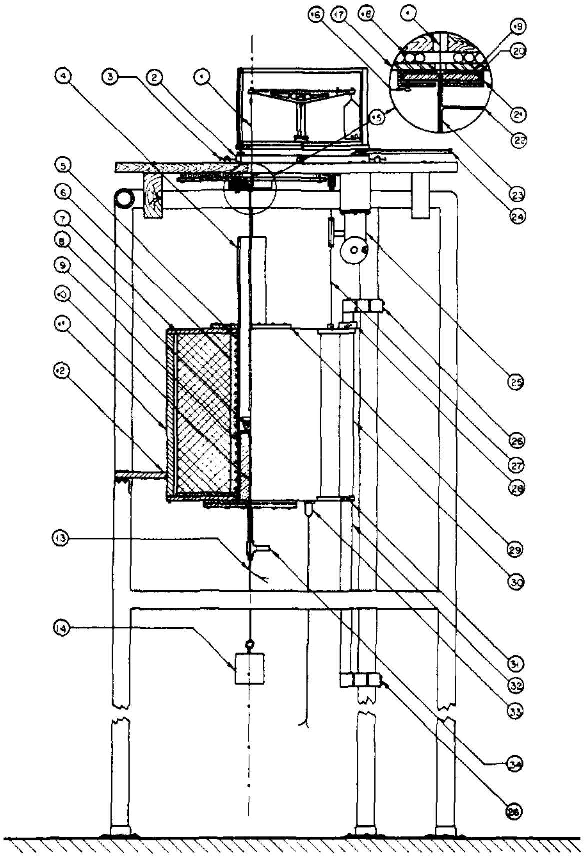

Fig. 1.—Density apparatus: 1, platinum suspension wire; 2, lateral adjustment supporting frame; 3, lateral adjustment screw (one of four, 90° apart); 4, silica furnace tube; 5, nichrome resistance winding; 6, alundum winding insulation; 7, vermiculite insulation; 8, platinum sinker; 9, insulating fire-brick crucible platform; 10, silica thermocouple tube; 11, furnace guide bar; 12, furnace guide lug; 13, chromel–alumel thermocouple wires; 14, lead counterweight (one of two, 180° apart); 15, enlarged cutaway of anti-condensation tube support and alignment assembly; 16, angular adjustment screw for anti-condensation tube (one of three, 120° apart); 17, water-cooled radiation shield; 18, cooling coil; 19, sponge rubber tension pad; 20, hard rubber supporting disc for anti-condensation tube; 21, brass alignment band; 22, line to dry air supply; 23, silica anti-condensation tube; 24, cooling water inlet; 25, elevating mechanism reduction gear; 26, elevating mechanism guide rod clamps; 27, elevating mechanism cable; 28, vertical level locking ring; 29, asbestos clamp ring; 30, elevating mechanism guide tube; 31, furnace position lock screw; 32, elevating mechanism guide rod; 33, power leads to furnace winding; 34, lead to dry air supply.

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