JOURNAL

OF

THE CHEMICAL SOCIETY.

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1. *Densities of Molten Inorganic Nitrate Mixtures.*

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DENSITIES of molten inorganic salts were measured by Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1), using a hydrostatic method, but he confined his attention to pure substances; Sandonnini (*Gazzetta*, 1920, **50**, i, 289) reported the densities at 350° and 400° of three mixtures of sodium nitrate with potassium nitrate, but no further information is available upon molten salt mixtures. Such data being of value, we have accurately determined densities, over a considerable temperature range, for various systems of nitrates, all of which have been examined by us in other ways (Laybourn and Madgin, J., 1933, 236).

EXPERIMENTAL.

Hydrostatic measurements are not convenient in operation, and a simple and exact method, similar to that employed by Matuyama (*Sci. Rep. Imp. Univ. Tôhoku,* 1929, **18**, 19) for molten metals, has been devised. It consists essentially in weighing a known volume of liquid in a bulb calibrated for volumes.

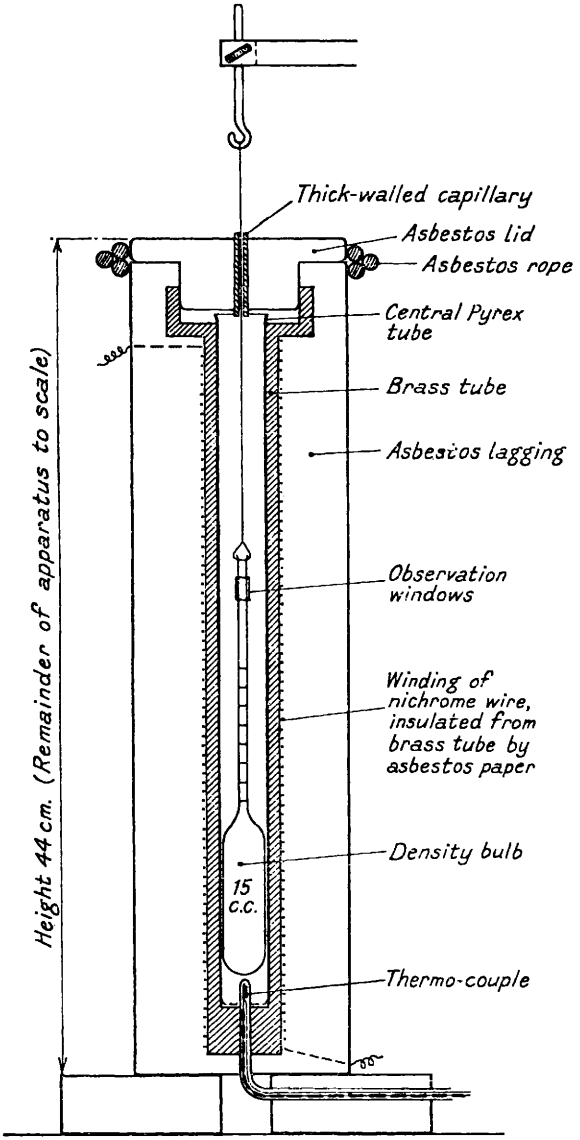
The bulb (see Fig. 1) was of Pyrex glass, and had a long narrow flanged neck graduated with eight annular marks approximately 1 cm. apart. The narrow neck (diam. 4 mm.) is essential for accuracy of volume measurement but it is difficult to fill such a bulb with liquid by ordinary methods without formation of air-locks. A pipette of special design (see below) was therefore used to transfer the molten substances from the fusion furnace to the density bulb.

Materials used were purified as described in earlier papers (*loc. cit.*), and the mixtures were fused in a Pyrex glass tube, heated electrically to a temperature about 25° above the freezing point of the particular mixture used. The transferring pipette, also of Pyrex glass, slightly exceeded the density bulb in volume, and had a delivery tube of small bore, similar in length to the neck of the density bulb, drawn to a fine tip (0·5 mm. diam.). In actual use, the pipette was preheated within the fusion tube above the melt, and liquid was then drawn in by slight suction from the pump, and retained by closing the top of the pipette with the finger. On raising the pipette from the fusion furnace, the liquid at the tip of the delivery tube quickly solidified, thus preventing leakage when this tube was introduced into the neck of the density bulb, but the main bulk of liquid remained molten.

The density bulb was suspended at the flange of the neck from a loop of fine nichrome wire in a preheating furnace, made by winding two concentric glass tubes with resistance wire. In this furnace the operation of filling could be clearly observed. The bulb was preheated to a temperature above the freezing point of the mixture under examination and the delivery tube of the charged pipette was then introduced into the neck. In a few seconds the solid seal melted and the molten substance could be run into the bulb under control and without the formation of air-locks or the contamination of the upper parts of the long neck. Sufficient liquid was introduced to fill the bulb to about the second graduation mark and the bulb was then transferred to the furnace used for the actual density measurements.

Fig. 1 shows a section of the furnace. It consists essentially of a thick brass tube wound with resistance wire and well lagged with asbestos. The metal serves to equalise temperature throughout the furnace. A thermocouple enters through a small hole in the base, and temperature measurements are made with the other junction of the couple immersed in the vapour of boiling sulphur, using an accurate millivoltmeter capable of giving temperatures to ± 0·5°. The top of the furnace is closed by a thick asbestos lid and, when in use, is further sealed with a winding of asbestos rope. The lid carries a small length of capillary tubing through which the wire suspending the density bulb is threaded after introduction of the bulb into the furnace. The top end of the wire is attached to a glass hook whose height can be adjusted by means of a clamp. The furnace is also provided with two small diametrically opposed windows (1 cm. × ¼ cm.), and a central Pyrex-glass lining which prevents any possible local cooling effect by these apertures.

Fig. 1.



In an actual determination of the density of a salt mixture, the temperature was adjusted (by means of external resistance) to a suitable point, and sufficient time allowed (8 hours) for the filled density bulb, within the furnace, to attain this temperature. The bulb was then raised, by adjustment of the height of the suspension hook, until the meniscus and one definite graduation mark were visible with a cathetometer through the observation windows. A strong light, placed behind the furnace, enabled the heights of the meniscus and graduation mark to be easily read. The heights of both top and bottom of the meniscus were taken in order that a correction for the volume of the meniscus might be applied. When raising the bulb, a small length of the suspension wire was exposed to a lower temperature and the consequent contraction affected the meniscus height slightly; the cathetometer readings were therefore not made until 30 minutes after the glass hook had been raised; repeated readings were then found to be constant.

Calibration of Bulb, and Calculation of Density.—The internal diameter of the tubing used to make the necks of the density bulbs was measured with a travelling microscope, and the exact distances between the neck graduations on the various bulbs were measured with a cathetometer. The bulb was now immersed in an ice-bath at 0°, and pure mercury introduced until the meniscus stood at a suitable height on the graduated portion of the neck. The height of the meniscus above the adjacent graduation was read and thus its height above the lowest graduation could be found. The weight of the mercury was subsequently determined. With different amounts of mercury, the whole graduated portion of the bulb neck was calibrated in this way. The density of mercury at 0° was used to calculate the volumes corresponding to the various heights above the lowest graduation, a correction being applied for the volume of the mercury meniscus in the course of the subsequent density calculations. Similar calibrations were made for a series of temperatures up to 300°, the density furnace being used as a heating bath, and in this way the coefficient of cubical expansion of the glass bulb could be determined. We found this coefficient to be 96×10^{-7} and to be independent of the temperature : this information enabled the volume corresponding to any height at any temperature to be calculated rapidly from the graph showing heights plotted against volumes for 0°. The density of mercury at 0° was taken as 13·5951.

When the density of a salt mixture was determined, the meniscus height was read for several temperatures, and the charged density bulb then removed from the furnace and allowed to cool in a desiccator before weighing. The temperatures chosen for determinations of the densities of molten salt mixtures were within about 10° of the respective freezing points, in the first instance. Thereafter temperatures were raised progressively to as much as 200° above the freezing points, but this range of variation was frequently restricted by decomposition (*e.g.*, in mixtures containing lead nitrate).

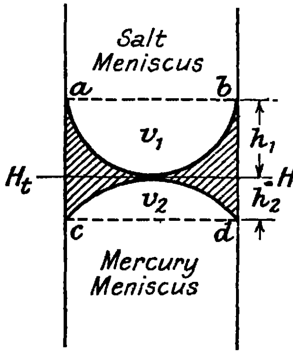
Solidified salts were easily removed from bulbs by means of a fine jet of hot water. In order to discover if molten nitrates had any effect on the glass, bulbs were filled with various mixtures and kept at 350—450° in the density furnace for 6 days: the loss in weight of any of the bulbs was never as high as the possible error in weighing, and in most cases no loss at all could be detected.

The density of a mixture of mass m g. at a temperature $t°$ is $D_t = m/V_t$, where V_t is the true volume of the liquid; V_t can be calculated from H_t, the observed height meniscus reading, since the latter corresponds to a volume v_0, on the calibration graph relating to conditions at 0°; v_0 is corrected to $t°$ by $v_t = v_0(1 + 96 \times 10^{-7}t)$ and v_t requires correction for meniscus volume as follows.

In Fig. 2, v_1 represents the meniscus volume for a salt melt and v_2 that for mercury when each is at a height H_t and bounded by ab and cd respectively. By considering v_1 and v_2 as caps of spheres, they can be calculated from measurements of the respective heights, h_1 and h_2, and r, the radius of the containing tube. The general expression for such volumes is $v = \pi/6 \,.\, (3r^2h + h^3)$; πr^2h_1 is the volume between H_t and ab, and πr^2h_2 that between H_t and cd. Thus the following relation holds: $V_t = v_t + (\pi r^2h_1 - v_1) + (\pi r^2h_2 - v_2)$ and, on substitution for v_1 and v_2, $V_t = v_t + \pi/6 \,.\, [3r^2(h_1 + h_2) - (h_1^3 + h_2^3)]$.

The systems investigated in the present work were binary mixtures of potassium nitrate with sodium, lead, barium, and strontium nitrates, sodium nitrate with lead nitrate, and certain ternary mixtures of the nitrates of potassium, barium, and strontium. The only pure substances which could be fused were potassium and sodium nitrates.

FIG. 2.

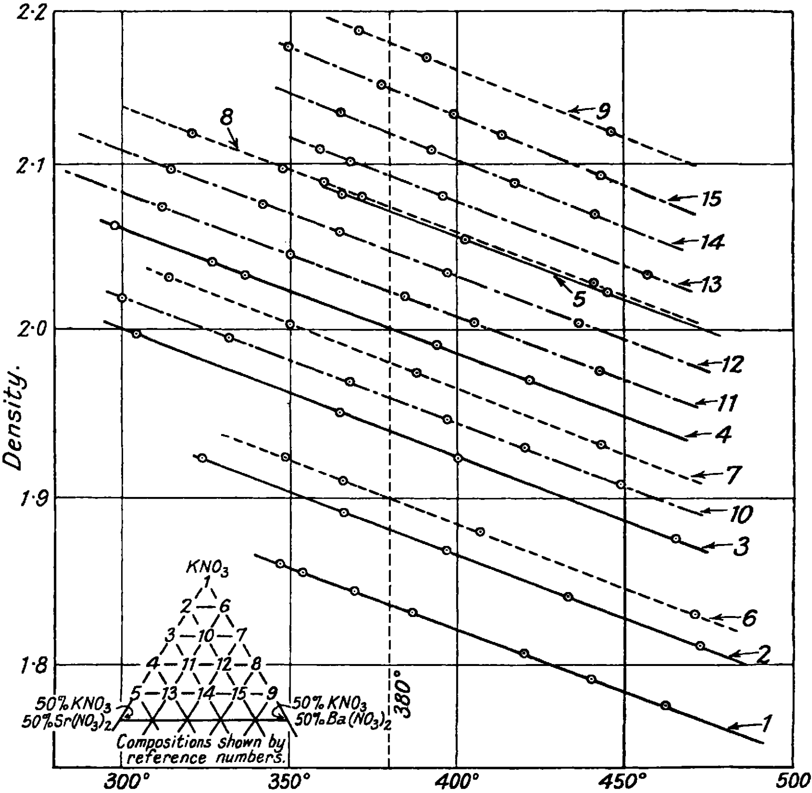


Results and Discussion.—The results of the various measurements made are in the table. In all cases density varies linearly with temperature, either for a pure substance or for any one of the mixtures. Fig. 3 shows density plotted against temperature for a number of binary and ternary mixtures and, in each example, a straight line is obtained. Such behaviour seems quite general and, in the results now reported, the maximum deviations of the densities from the corresponding straight lines never exceeded ± 0·001, which is the limiting error claimed for these results.

Data for the study of density–composition curves at a given temperature can be obtained by drawing an isothermal across a set of lines, covering the necessary range of composition for the particular system (cf. 380° isothermal, Fig. 3). To test whether an isothermal density–composition curve follows the mixture law, it is necessary that an orthomeric function should be examined, and this requires that either density should be plotted against composition by volume or specific volume plotted against composition by weight (cf. MacFarlane and Wright, J., 1933, 114). The specific volume is the most suitable quantity to use here, since the densities of those pure substances which were infusible are not known.

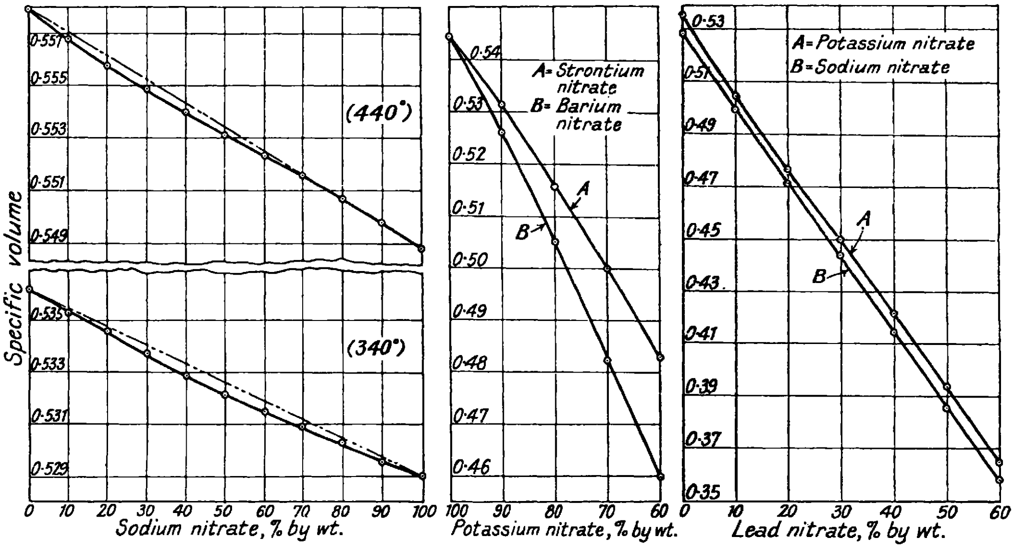
Specific volumes, calculated from the corresponding densities, are plotted against composition by weight for five binary systems in Fig. 4; the relevant temperatures are shown. Only in the system potassium nitrate–sodium nitrate could a full range of composition be examined, and the deviation from the straight line (mixture law) is slight and decreases as the temperature rises. Both curves are convex towards the composition axis, but the higher-temperature curve is a straight line for part of the range. An exactly

FIG. 3.



Potassium nitrate with strontium and barium nitrates. Variations of liquid densities with temperature.

FIG. 4.



(1)

Potassium nitrate with sodium nitrate.

(2)

Potassium nitrate with strontium or barium nitrate (380°).

(3)

Lead nitrate with potassium or sodium nitrate (340°).

similar curve to the latter is shown for the system potassium nitrate–lead nitrate, while the system sodium nitrate–lead nitrate gives a straight line.

The other two systems [Fig. 4 (2)] differ only very slightly from the straight line but in the opposite sense from the above, *i.e.*, the curves are concave towards the composition axis. The five binary systems have been examined by us previously (J., **1933**, 236 and earlier references) and, whilst potassium and sodium nitrates form a continuous series of solid solutions, the remaining four systems are of the simple eutectic type. This classification is in no way indicated by the present results either by the nature or the extent of the deviations from the mixture law; indeed, the deviations are much too small to suggest any conclusions.

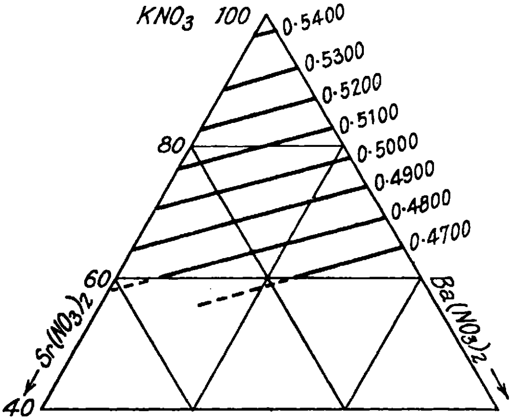
The specific volume–composition relations for the three-component system potassium nitrate–strontium nitrate–barium nitrate have been examined for the range of composition prescribed by decomposition (see inset, Fig. 3). The densities on the constant-temperature line (380°) in Fig. 3 were converted into specific volumes, which were as follows (Nos. 1—15 refer to compositions as in Fig. 3):

No.	1	2	3	4	5	6	7	8
Spec. vol.	0·5446	0·5316	0·5157	0·4998	0·4828	0·5262	0·5051	0·4823
No.	9	10	11	12	13	14	15	
Spec. vol.	0·4599	0·5107	0·4943	0·4887	0·4778	0·4722	0·4665	

These results were used to construct Fig. 5, where points representing mixtures of equal specific volume are joined. The method of construction was similar to that employed by us in deducing liquidus isothermal diagrams (J., **1932**, 2582). Lines of equal specific volume are straight, and make practically equal intercepts on the two sides of the triangle (Fig. 5), showing that the corresponding binary systems almost follow the mixture law. It is proposed to examine this type of diagram further.

Only for two pure components (potassium and sodium nitrates) were we able to obtain density–temperature curves, and our results never differ by more than 0·002 from the values calculated from the formulæ of Jaeger (*loc. cit.*); his freezing points for the two nitrates are respectively 1° and 2° lower than our values, so exact agreement is not to be expected.

Fig. 5.



The ternary system KNO_3–$Sr(NO_3)_2$–$Ba(NO_3)_2$. *Specific volumes of liquids at constant temperature* (380°). (*Lines of constant specific volume.*)

(Compositions are in weight percentages.)

1. *The system* KNO_3–$NaNO_3$.

100% KNO_3, 0% $NaNO_3$ (f. p. 340°).		90% KNO_3, 10% $NaNO_3$ (f. p. 307°).		80% KNO_3, 20% $NaNO_3$ (f. p. 277°).		70% KNO_3, 30% $NaNO_3$ (f. p. 250°).		60% KNO_3, 40% $NaNO_3$ (f. p. 229°).		50% KNO_3, 50% $NaNO_3$ (f. p. 227°).	
D_t.	t.	D_t.	t.	D_t.	t.	D_t.	t.	D_t.	t.	D_t.	t.
1·860	347°	1·887	314°	1·907	291°	1·934	258°	1·948	242°	1·943	252°
1·855	354	1·868	340	1·877	332	1·914	286	1·920	281	1·905	305
1·844	369	1·852	362	1·850	369	1·890	318	1·892	320	1·883	335
1·831	387	1·829	394	1·825	404	1·859	360	1·882	333	1·838	398
1·806	420	1·802	431	1·797	442	1·825	407	1·842	388	1·797	455
1·792	440					1·797	446	1·796	452		
1·776	462										

40% KNO_3, 60% $NaNO_3$ (f. p. 241°).		30% KNO_3, 70% $NaNO_3$ (f. p. 260°).		20% KNO_3, 80% $NaNO_3$ (f. p. 279°).		10% KNO_3, 90% $NaNO_3$ (f. p. 295°).		0% KNO_3, 100% $NaNO_3$ (f. p. 310°).			
D_t.	t.	D_t.	t.	D_t.	t.	D_t.	t.	D_t.	t.	D_t.	t.
1·944	254°	1·934	270°	1·922	289°	1·910	310°	1·904	318°		
1·924	282	1·911	302	1·874	357	1·887	342	1·887	344		
1·876	348	1·889	333	1·818	437	1·842	406	1·876	360		
1·823	421	1·850	388			1·806	459	1·864	378		
1·809	442	1·799	460					1·848	402		
								1·839	415		
								1·810	458		

2. *The system* KNO_3–$Pb(NO_3)_2$.

90% KNO_3, 10% $Pb(NO_3)_2$ (f. p. 328°).		80% KNO_3, 20% $Pb(NO_3)_2$ (f. p. 312°).		70% KNO_3, 30% $Pb(NO_3)_2$ (f. p. 290°).		60% KNO_3, 40% $Pb(NO_3)_2$ (f. p. 258°).		50% KNO_3, 50% $Pb(NO_3)_2$ (f. p. 219°).		40% KNO_3, 60% $Pb(NO_3)_2$ (f. p. 271°).	
1·983	332	2·110	320	2·255	302	2·430	274	2·651	230	2·805	276°
1·978	340	2·095	338	2·235	330·5	2·413	292	2·619	261	2·791	288·5
1·961	360	2·072	368	2·219	352	2·396	312	2·606	275	2·761	318·5
1·944	387	2·058	386·5	2·203	372	2·368	344	2·589	292	2·736	345
1·922	418·5	2·044	405	2·190	390	2·350	363	2·529	353		
						2·337	377	2·516	366		

3. *The system* $NaNO_3$–$Pb(NO_3)_2$.

90% $NaNO_3$, 10% $Pb(NO_3)_2$ (f. p. 304°).		80% $NaNO_3$, 20% $Pb(NO_3)_2$ (f. p. 297°).		70% $NaNO_3$, 30% $Pb(NO_3)_2$ (f. p. 288°).		60% $NaNO_3$, 40% $Pb(NO_3)_2$ (f. p. 278°).		50% $NaNO_3$, 50% $Pb(NO_3)_2$ (f. p. 301°).		40% $NaNO_3$, 60% $Pb(NO_3)_2$ (f. p. 335°).	
2·022	311	2·145	305	2·283	296	2·457	287	2·620	306	2·792	338
2·005	335	2·133	321	2·273	308	2·437	310	2·600	328	2·779	349
1·993	352	2·113	348	2·249	341	2·432	316	2·585	343	2·764	363
1·968	388	2·100	364	2·228	371	2·401	351	2·556	373		
1·960	400	2·084	387	2·209	398	2·368	391				
1·940	429	2·060	419								

4. *The system* KNO_3–$Sr(NO_3)_2$.

90% KNO_3, 10% $Sr(NO_3)_2$ (f. p. 322°).		80% KNO_3, 20% $Sr(NO_3)_2$ (f. p. 295°).		70% KNO_3, 30% $Sr(NO_3)_2$ (f. p. 294°).		60% KNO_3, 40% $Sr(NO_3)_2$ (f. p. 361°).	
1·923	324	1·997	304	2·062	298	2·082	366
1·891	366	1·951	365·5	2·040	327	2·054	402
1·868	397	1·924	400	2·033	337	2·022	445
1·841	433	1·876	465	1·991	394		
1·810	474			1·970	421		

5. *The system* KNO_3–$Ba(NO_3)_2$.

90% KNO_3, 10% $Ba(NO_3)_2$ (f. p. 331°).		80% KNO_3, 20% $Ba(NO_3)_2$ (f. p. 307°).		70% KNO_3, 30% $Ba(NO_3)_2$ (f. p. 301°).		60% KNO_3, 40% $Ba(NO_3)_2$ (f. p. 360°).	
1·924	349	2·031	314	2·118	321	2·179	371
1·911	366	2·003	350	2·096	348	2·163	391
1·880	407	1·974	388	2·079	371	2·119	446
1·830	471	1·932	443	2·026	441		

6. *The ternary system* KNO_3–$Sr(NO_3)_2$–$Ba(NO_3)_2$.

80% KNO_3, 10% $Sr(NO_3)_2$, 10% $Ba(NO_3)_2$ (f. p. 296°).		70% KNO_3, 20% $Sr(NO_3)_2$, 10% $Ba(NO_3)_2$ (f. p. 283°).		70% KNO_3, 10% $Sr(NO_3)_2$, 20% $Ba(NO_3)_2$ (f. p. 287°).		60% KNO_3, 30% $Sr(NO_3)_2$, 10% $Ba(NO_3)_2$ (f. p. 350°).		60% KNO_3, 20% $Sr(NO_3)_2$, 20% $Ba(NO_3)_2$ (f. p. 346°).		60% KNO_3, 10% $Sr(NO_3)_2$, 30% $Ba(NO_3)_2$ (f. p. 347°).	
2·018	300	2·074	312	2·097	315	2·109	359	2·130	365	2·168	350
1·996	332	2·046	350	2·076	342	2·101	368	2·108	392	2·146	378
1·969	368	2·020	384	2·059	365	2·080	396	2·089	417	2·129	399
1·947	397	2·004	405	2·034	397	2·033	456	2·070	441	2·118	413
1·930	420	1·976	442	2·004	436					2·094	443
1·908	449										

SUMMARY.

(1) A method is described for the exact determination of the densities of molten salts and salt mixtures.

(2) Density values for various systems of inorganic nitrates have been obtained over a range of temperature (about 150°), starting near the respective freezing points.

(3) Density varies linearly with temperature for each of the mixtures studied by us.

(4) Isothermal specific volume–composition curves are found to differ only slightly from the values required by the mixture law.

We are indebted to the Research Committee of this college for a grant.

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[*Received, August* 15*th,* 1933.]