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DENSITY AND VISCOSITY OF SEVERAL MOLTEN FLUORIDE MIXTURES

Stanley Cantor

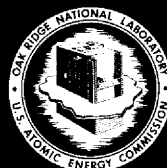
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DENSITY AND VISCOSITY OF SEVERAL MOLTEN
FLUORIDE MIXTURES

Stanley Cantor

March 1973

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
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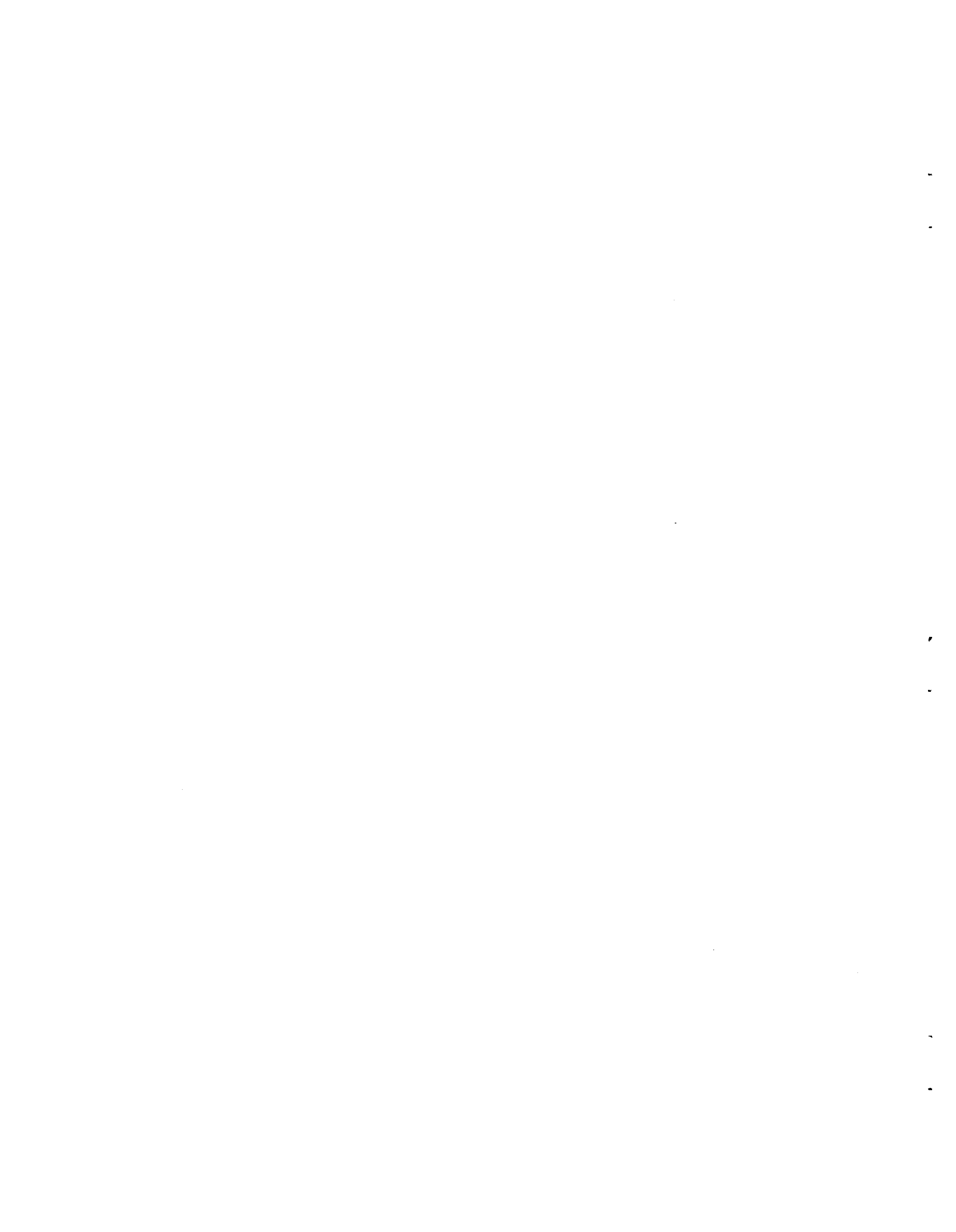
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DENSITY AND VISCOSITY OF SEVERAL MOLTEN FLUORIDE MIXTURES

Stanley Cantor

ABSTRACT

Using a dilatometric method, densities were determined for the following molten salts:

LiF-BeF₂ (66-34 mole %)
LiF-BeF₂-ThF₄ (70.1-23.9-6.0, 70-18-12, 70-15-15 mole %)
LiF-BeF₂-ZrF₄ (64.7-30.1-5.2 mole %)
LiF-BeF₂-ZrF₄-UF₄ (64.79-29.96-4.99-0.26 mole %)
NaBF₄-NaF (92-8 mole %)
KNO₃

The last salt was measured to assure the accuracy of the method; the densities measured for KNO₃ agreed within 0.15% with critically evaluated densities obtained by Archimedean methods.

For the fluorides, molar volumes obtained from the density measurements agreed within 2% with volumes calculated from additive contributions of the components. The expansivities of three LiF-BeF₂-ThF₄ mixtures were practically identical, $2.5 \times 10^{-4}/^{\circ}\text{C}$.

Density-temperature curves from 25-700°C for LiF-BeF₂-ThF₄ (72-16-12 mole %) and for NaBF₄-NaF (92-8 mole %) were derived from room-temperature pycnometric determinations and from estimated expansivities of the solid salts. The calculated expansion, upon melting, for the former is 7%, for the latter 8%.

Viscosities of three salt mixtures were determined by oscillating-cup methods:

LiF-BeF₂-ThF₄ (72.7-15.7-11.6, 70.1-23.9-6.0 mole %)
NaBF₄-NaF (92-8 mole %)

Viscosity measurements were conducted at Mound Laboratory, Miamisburg, Ohio, using capsules and samples prepared at ORNL. The viscosities of the two melts composed of LiF, BeF₂, and ThF₄ were analogous to viscosities reported for similar mixtures containing UF₄ instead of ThF₄.

DENSITY OF MOLTEN SALTS

The objectives of this investigation were: (a) to measure, with high accuracy, densities and expansivities of several molten fluoride mixtures that are significant to molten-salt reactors, (b) to derive additive molar volume contributions which can serve to predict densities in LiF-BeF₂-(Th,U)F₄ molten solutions, (c) to estimate density changes upon melting of the fuel-carrier and coolant salts of the molten-salt breeder reactor.

Experimental

Apparatus and Procedures: Densities were determined in a nickel dilatometer (Figure 1), the details of which have been previously described.^{1,2} In the apparatus a metal probe detects the changes in liquid level in the neck of a volume-calibrated metal vessel. The escape of vapor is prevented by a Teflon stopper, which also permits vertical displacement of the probe. When the probe contacts the liquid surface, a vacuum-tube voltmeter changes from an open circuit reading to a detectable resistance. The probe height is measured to ± 0.02 mm with a cathetometer. Through a side arm in the neck of the vessel, an inert insoluble gas (argon) is introduced to suppress bubbles in the melt. By taking measurements at argon pressures of approximately 5 atm, entrapped gas bubble volumes were reduced to less than 0.1% of the liquid sample.

After completing measurements at elevated temperatures, the contents of the vessel were removed and weighed to be certain that weight changes had been negligible. For any sample measured, weight changes never exceeded 0.05%. After each run, the dilatometric vessel was recalibrated at room temperature with distilled water. The recalibrations indicated that the nickel vessels sustained permanent expansions of about 0.2%.

Melt temperatures were controlled to $\pm 0.2^\circ$ by regulating the furnace with a Leeds and Northrup Speedomax proportional controller. Temperatures of the melt were determined with Pt-Rh thermocouples previously calibrated by the National Bureau of Standards; these thermocouples are stated to be accurate within 0.5° in the temperature range (400-820°C) of measurement.

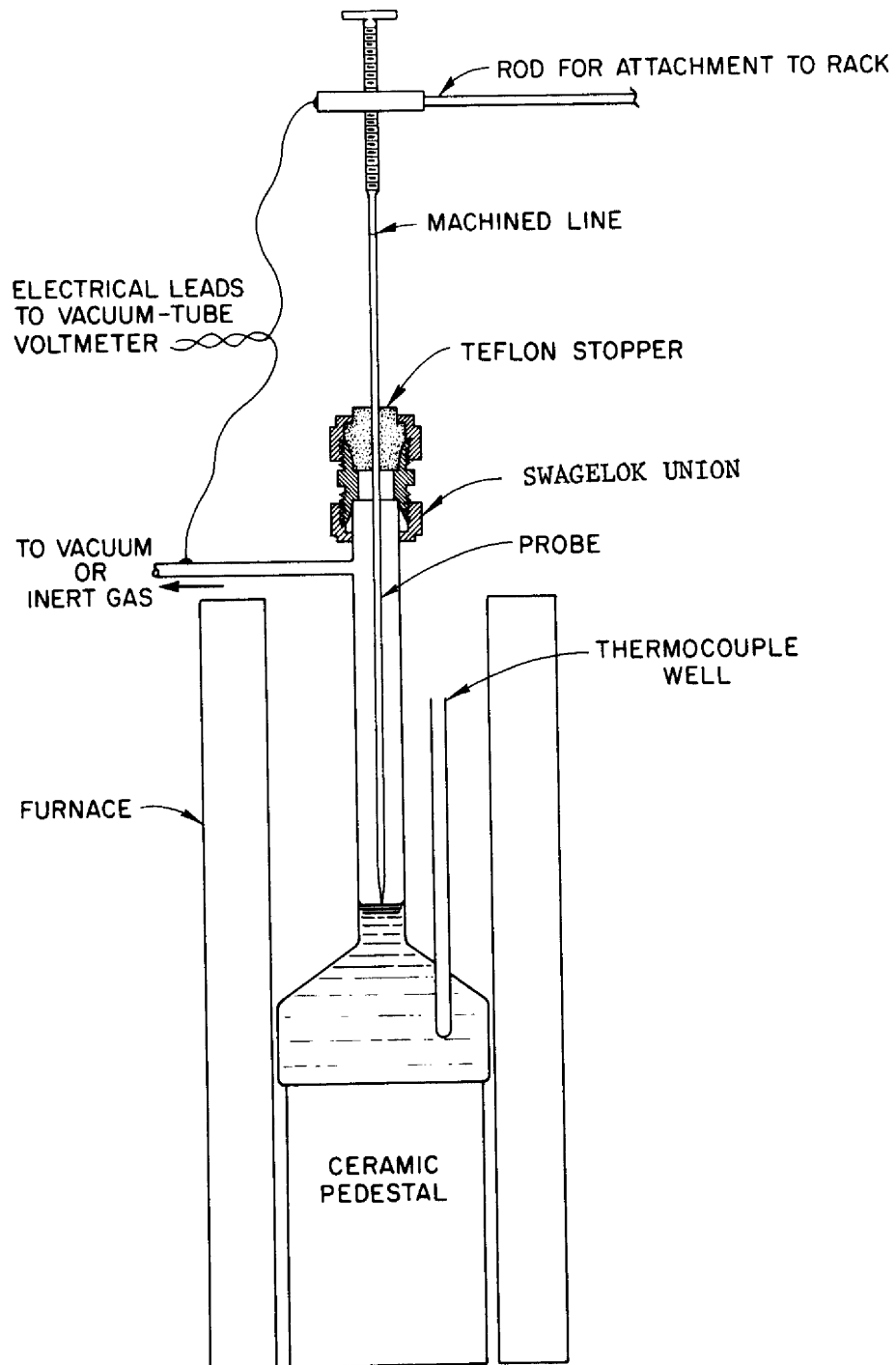


Fig. 1. Dilatometer for Measuring Volume of Molten Salts. The part of the probe above the Teflon stopper is longer than indicated in the figure.

Materials

The salt mixtures, LiF-BeF₂ (66-34 mole %) and LiF-BeF₂-ZrF₄ (64.7-30.1-5.2 mole %), were supplied by J. H. Shaffer, ORNL, from batches that had been sparged by H₂-HF gaseous treatment.³ By adding purified, crystalline LiF⁴ and UF₄⁵ to the latter, we prepared LiF-BeF₂-ZrF₄-UF₄ (64.79-29.96-4.99-0.26 mole %). In the order given above, the three compositions corresponded to the MSRE coolant, carrier salt, and fuel salt mixtures.

Mixtures of LiF-BeF₂-ThF₄ (used in both density and viscosity measurements) were constituted from LiF-BeF₂ (66-34 mole %), crystalline LiF, and LiF-ThF₄ mixtures. The LiF-ThF₄, retained from a previous density study,⁴ had been stored in a vacuum desiccator. The mixture, NaBF₄-NaF (92-8 mole %), was constituted from the purified components.^{2,6}

Analytical-grade KNO₃ (J. T. Baker Chemical Co., Phillipsburg, N.J.) was used as received. Measurements of the salt were carried out primarily for checking the accuracy of the dilatometric method used in the present investigation.

Argon gas, used for suppressing bubbles in the melts (see above), was obtained from Airco, Chester, W. Va. The gas was shown by mass spectrographic analysis to exceed 99.9% in purity. Prior to entry into the vessel, the gas was passed through molecular sieve to remove traces of moisture.

All salt loadings were carried out in a glovebox filled with helium. To insure that the liquid level reached into the neck of the vessel (see Figure 1), two loadings were usually required; after melting the initial charge of the salt, the vessel was returned to the glovebox for further loading.

Results

The densities of seven fluoride mixtures were measured over about a 200°C temperature range. The data are listed in Tables 1A - 1G; also included are the least-squares equation and the densities calculated from the equation. For each melt the plot of density versus temperature was linear. Data for KNO₃ are given in Table 2.

Table 1A. Density of LiF-BeF₂-ThF₄ (70.11-23.88-6.01 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
555.1	2.740 ₆	2.7395
571.9	2.727 ₆	2.7282
580.9	2.723 ₈	2.7222
596.7	2.711 ₁	2.7116
606.2	2.704 ₉	2.7052
621.3	2.694 ₀	2.6951
628.7	2.690 ₁	2.6901
646.8	2.677 ₄	2.6780
655.1	2.671 ₁	2.6724
673.2	2.660 ₆	2.6603
681.2	2.653 ₆	2.6549
707.4	2.639 ₈	2.6372

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 3.1118 - 6.707 \times 10^{-4} t \text{ (}^\circ\text{C)}.$$

Table 1B. Density of LiF-BeF₂-ThF₄ (70.06-17.96-11.98 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
533.2	3.394 ₂	3.3936
558.1	3.373 ₀	3.3735
561.4	3.369 ₈	3.3709
580.7	3.355 ₁	3.3553
588.8	3.348 ₁	3.3488
603.4	3.336 ₄	3.3370
615.0	3.327 ₈	3.3277
626.5	3.319 ₈	3.3184
640.2	3.306 ₀	3.3073
649.6	3.300 ₉	3.2997
673.1	3.283 ₇	3.2808
696.9	3.263 ₀	3.2616
721.0	3.241 ₂	3.2422
741.2	3.223 ₇	3.2259

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 3.8236 - 8.064 \times 10^{-4} t \text{ (}^\circ\text{C)}.$$

Table 1C. Density of LiF-BeF₂-ThF₄ (69.98 - 14.99 - 15.03 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
543.4	3.663 ₂	3.6634
556.7	3.649 ₃	3.6507
582.9	3.624 ₂	3.6258
608.5	3.602 ₁	3.6014
620.9	3.589 ₇	3.5896
633.7	3.578 ₈	3.5774
646.4	3.566 ₈	3.5653
659.1	3.554 ₁	3.5532
672.6	3.541 ₃	3.5403
698.9	3.516 ₃	3.5153
713.7	3.500 ₀	3.5012
730.2	3.483 ₆	3.4854
749.5	3.466 ₅	3.4671

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 4.1811 - 9.526 \times 10^{-4}t \text{ (}^\circ\text{C)}.$$

Table 1D. Density of LiF-BeF₂ (66-34 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
514.5	2.029 ₂	2.0284
540.5	2.015 ₃	2.0157
564.9	2.003 ₀	2.0038
590.5	1.991 ₅	1.9913
614.6	1.979 ₇	1.9795
616.0	1.978 ₅	1.9788
667.1	1.954 ₀	1.9539
719.5	1.928 ₅	1.9283
772.2	1.902 ₇	1.9025
794.7	1.891 ₁	1.8915
820.3	1.879 ₂	1.8790

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 2.2797 - 4.884 \times 10^{-4}t \text{ (}^\circ\text{C)}.$$

Table 1E. Density of LiF-BeF₂-ZrF₄ (64.7-30.1-5.2 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
452.0	2.278 ₀	2.2780
475.8	2.262 ₈	2.2642
501.0	2.249 ₇	2.2497
503.5	2.248 ₁	2.2483
523.4	2.237 ₁	2.2368
530.6	2.232 ₀	2.2326
546.9	2.223 ₅	2.2232
570.8	2.209 ₆	2.2094
594.9	2.196 ₀	2.1955
597.7	2.194 ₀	2.1939
619.0	2.182 ₂	2.1816
622.6	2.181 ₃	2.1796
642.2	2.169 ₆	2.1682
647.5	2.166 ₀	2.1652
666.5	2.154 ₇	2.1542
672.4	2.148 ₉	2.1508
698.2	2.135 ₀	2.1359
703.9	2.131 ₄	2.1327

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 2.5387 - 5.769 \times 10^{-4}t \text{ (}^\circ\text{C)}.$$

Table 1F. Density of LiF-BeF₂-ZrF₄-UF₄ (64.79-29.96-4.99-0.26 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
524.3	2.257 ₆	2.2587
571.1	2.231 ₉	2.2324
617.2	2.205 ₇	2.2064
625.6	2.205 ₄	2.2017
640.7	2.192 ₈	2.1932
664.1	2.180 ₀	2.1801
697.5	2.162 ₆	2.1613
715.8	2.149 ₃	2.1510
761.1	2.125 ₁	2.1256

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 2.5533 - 5.620 \times 10^{-4}t \text{ (}^\circ\text{C)}.$$

Table 1G. Density of NaBF₄-NaF (92-8 mole %)

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
399.5	1.965 ₀	1.9680
423.4	1.950 ₂	1.9511
448.0	1.936 ₄	1.9336
471.9	1.918 ₀	1.9166
494.6	1.901 ₃	1.9004
495.8	1.900 ₇	1.8996
519.8	1.882 ₂	1.8825
543.4	1.866 ₄	1.8657
567.4	1.846 ₆	1.8487
590.8	1.831 ₄	1.8320

^aFrom the least-squares equation:

$$(\text{g/cm}^3) = 2.2521 - 7.110 \times 10^{-4} t \text{ (}^\circ\text{C)}.$$

Table 2. Density of KNO_3

Temperature (°C)	Density (g/cm ³)	
	Experimental	Calculated ^a
343.6	1.871 ₆	1.8695
360.4	1.857 ₉	1.8571
369.8	1.850 ₃	1.8501
375.2	1.845 ₆	1.8461
384.0	1.839 ₁	1.8395
384.6	1.838 ₀	1.8391
386.4	1.837 ₄	1.8378
389.0	1.834 ₈	1.8358
395.8	1.830 ₇	1.8308
399.5	1.827 ₅	1.8280
403.1	1.823 ₉	1.8253
412.6	1.817 ₁	1.8183
414.8	1.817 ₉	1.8167
416.8	1.818 ₅	1.8152
425.9	1.806 ₈	1.8084
426.0	1.809 ₀	1.8083
437.7	1.800 ₀	1.7996
445.8	1.793 ₃	1.7936
450.9	1.789 ₄	1.7898
474.0	1.772 ₁	1.7727
499.4	1.754 ₃	1.7538
511.8	1.744 ₃	1.744 ₆
537.9	1.725 ₂	1.725 ₂
560.3	1.708 ₇	1.708 ₆
586.3	1.689 ₃	1.6893
611.9	1.670 ₇	1.6702

^aFrom the least-squares equation:

$$\rho(\text{g/cm}^3) = 2.1248 - 7.428 \times 10^{-4} t \text{ (}^\circ\text{C)}.$$

The standard error in density was approximately 0.001 g/cm^3 , corresponding to about 0.05%. Other sources of error (creep sustained by the vessel, bubble volume, small amounts of salt condensed on the upper neck of the vessel) increase the total error to $\pm 0.3\%$. This percentage error was determined by comparing our results with those of Bloom *et al.*⁷ Janz,⁸ in his critical review, judges the uncertainty in Bloom's results to be about 0.2%; our results differ from those of Bloom by 0.15%. The density-temperature equations for KNO_3 are:

$$\begin{aligned} \rho(\text{g/cm}^3) &= 2.116 - 7.29 \times 10^{-4} t \text{ (}^\circ\text{C)} && \text{Bloom et al.}^7 \\ \rho(\text{g/cm}^3) &= 2.125 - 7.43 \times 10^{-4} t \text{ (}^\circ\text{C)} && \text{our results.} \end{aligned}$$

Discussion

Additive Molar Volumes

The simplest, and often quite successful, way for estimating the density of solutions is to assume that the volume of a mixture is the sum of additive contributions of the component compounds. The additive contributions are usually available from density measurements of the components; the density - and hence the molar volumes, of LiF ,⁴ ThF_4 ,⁹ and BeF_2 ¹⁰ have been reported by the author. At 550 and 700°C, the molar volumes obtained from these investigations are:

	Volume (cm^3)	
	<u>550°C</u>	<u>700°C</u>
LiF	13.24	13.77
BeF ₂	24.0	24.2
ThF ₄	46.15	47.00

Molar volumes of the three $\text{LiF-BeF}_2\text{-ThF}_4$ mixtures and the LiF-BeF_2 mixture were calculated from the values above; the calculated and experimental molar volumes are compared in Table 3. Calculated volumes are approximately one percent greater than experimental values. The good agreement is probably due to the small sizes and low polarizabilities of the ions which comprise these mixtures.

The concentrations of ZrF_4 and UF_4 in the two mixtures studied were not large enough to test whether or not their molar volume contributions

Table 3. Molar^a Volumes of Fluoride Mixtures

Composition (mole fraction, N_i)			Molar Volumes (cm^3)					
			550°C			700°C		
LiF	BeF ₂	ThF ₄	Exptl.	Calcd. ^b	Diff. ^c	Exptl.	Calcd. ^b	Diff. ^c
0.7011	0.2388	0.0601	17.47	17.7 ₉	1.89%	18.14	18.2 ₆	0.88%
0.7006	0.1796	0.1198	18.79	19.1 ₁	1.65%	19.49	19.6 ₂	0.56%
0.6998	0.1499	0.1503	19.55	19.8 ₀	1.79%	20.34	20.3 ₃	-0.15%
0.66	0.34	-	16.46	16.9 ₀	2.67%	17.08	17.3 ₂	1.41%
LiF	BeF ₂	ZrF ₄						
0.647	0.301	0.052	17.84	18.1 ₈	1.91%	18.56	18.6 ₀	0.22%
0.6479	0.2996	0.0499 +0.0026UF ₄	17.85	18.1 ₈	1.85%	18.54	18.6 ₉	0.81%
NaBF ₄	NaF							
0.92	0.08		56.08	56.1 ₁	0.05%	59.49 ^d	59.7 ₁	0.37%

^aA mole of salt mixture is defined: $\bar{M} = \sum N_i M_i$, where \bar{M} is molar mass, N_i is mole fraction of component i , M_i is gram-formula weight of component i .

^bCalculated from the equation $\bar{V} = \sum N_i V_i$, where \bar{V} and V_i are, respectively, molar volumes of the mixture and of component i , both at the same temperature. Values of V_i given in the Discussion.

^c $100 \times \left(\frac{\text{Calculated volume minus experimental volume}}{\text{experimental volume}} \right)$.

^dExtrapolated.

were additive. Nonetheless, the molar volumes at 550 and 700°C of the mixtures containing these components were calculated using, in addition to the LiF and BeF₂ molar volume given above, the following:

$$\begin{aligned} \text{ZrF}_4: & 46 \text{ cm}^3 \text{ at } 550^\circ\text{C}; \quad 48 \text{ cm}^3 \text{ at } 700^\circ\text{C} \\ \text{UF}_4: & 45.1 \text{ cm}^3 \text{ at } 550^\circ\text{C}; \quad 46.1 \text{ cm}^3 \text{ at } 700^\circ\text{C} \end{aligned}$$

The ZrF₄ volumes were derived (not measured directly) from the densities of alkali fluorides - ZrF₄ melts studied by Mellors and Senderoff.¹¹ Molar volumes for UF₄ are extrapolated from densities measured by Kirshenbaum and Cahill.¹²

For NaBF₄-NaF (92-8 mole %), the observed molar volume would not be expected to deviate from the additive value. Table 3 shows that volumes calculated from additive contributions agree within 0.4% with experimental results. The additive contributions^{2,13} are:

$$\begin{aligned} \text{NaBF}_4: & 59.35 \text{ cm}^3 \text{ at } 550^\circ\text{C}; \quad 63.20 \text{ cm}^3 \text{ at } 700^\circ\text{C} \\ \text{NaF} : & 18.82 \text{ cm}^3 \text{ at } 550^\circ\text{C}; \quad 19.62 \text{ cm}^3 \text{ at } 700^\circ\text{C} \end{aligned}$$

Expansivity

An interesting result, derived from the three mixtures containing ThF₄, is that the expansivity (fractional change of volume with temperature) did not seem to change with the concentrations of BeF₂ and ThF₄. Given that any fuel mixture for a molten-salt breeder reactor will contain about 70 mole % LiF, then the results suggest that the expansivity will be very close to $2.5 \times 10^{-4}/^\circ\text{C}$. The actual results were:

Salt Composition (mole %)	Expansivity, $\alpha = \frac{-1}{\rho} \frac{\partial \rho}{\partial T}$ at 600°C Units are (°C) ⁻¹
70.11 LiF, 23.88 BeF ₂ , 6.01 ThF ₄	$2.4_8 \times 10^{-4}$
70.06 LiF, 17.96 BeF ₂ , 11.98 ThF ₄	$2.4_1 \times 10^{-4}$
69.98 LiF, 14.99 BeF ₂ , 15.03 ThF ₄	$2.6_4 \times 10^{-4}$

Room-Temperature Density and Estimated Density Change, Upon Melting, of MSBR Fuel and Coolant Salts

This short investigation was conducted in order to provide reactor designers with a reasonable estimate of the density change, upon melting, of MSBR fuel and coolant salts.

Densities, at room temperature, were determined pycnometrically in a 25-cm³ Kimax "specific gravity bottle". The precise volume of the bottle was determined with distilled water. Cottonseed oil was used as the displacement liquid for the salts; the latter had been prefused and only relatively large (> 2 mm) crystalline fragments were used in the pycnometer. The results obtained were:

$$\begin{aligned} \text{LiF-BeF}_2\text{-ThF}_4 \text{ (72-16-12 mole \%)} &: 3.788_7 \text{ g/cm}^3 \\ \text{NaBF}_4 \text{ (100 mole \%)} &: 2.435_6 \text{ g/cm}^3 \end{aligned}$$

The pycnometric density of NaBF₄ was 3% less than the x-ray density of 2.5075 reported by Brunton.¹⁴

A density-temperature curve (Fig. 2) for LiF-BeF₂-ThF₄ (72-16-12 mole %) was constructed on the basis of the following assumptions: a) the pycnometrically determined density at 25°C is representative of the bulk density of the solid salt; b) the volume expansivity of the solid is $1 \times 10^{-4} / ^\circ\text{C}$, an estimate based on the value of this property in other salts;¹⁵ c) the density above the liquidus is reliably predicted from the additive molar volumes for LiF, BeF₂, and ThF₄ listed in the first part of this report. The calculations result in a predicted 7% decrease in density over the temperature range of melting (or freezing). Equations and other details are noted in Figure 2.

Two curves depicting the density-temperature behavior of MSBR coolant (92-8 mole % NaBF₄-NaF) are given in Figure 3. The solid lines refer to "theoretical" or x-ray densities. At 243°C and at 385°C, the dashed and solid lines coincide over a range of densities. The curves were generated with the assumptions: (i) at room temperature the molar volumes are additive, (ii) the density of this solid mixture is 3% less than the x-ray density (as was observed pycnometrically for pure NaBF₄); (iii) the temperature coefficient of density for the solid is a constant, $2.5 \times 10^{-4} / ^\circ\text{C}$; this coefficient corresponds to an expansivity of $1 \times 10^{-4} / ^\circ\text{C}$; (iv) the x-ray density of the high-temperature form of crystalline NaBF₄ is 2.17 g/cm³ at 243°C (the same as Bredig¹⁶ obtained at 265°C).

On the basis of these four assumptions and experimental data for the liquid, a density decrease of 8% upon melting is possible; however, a

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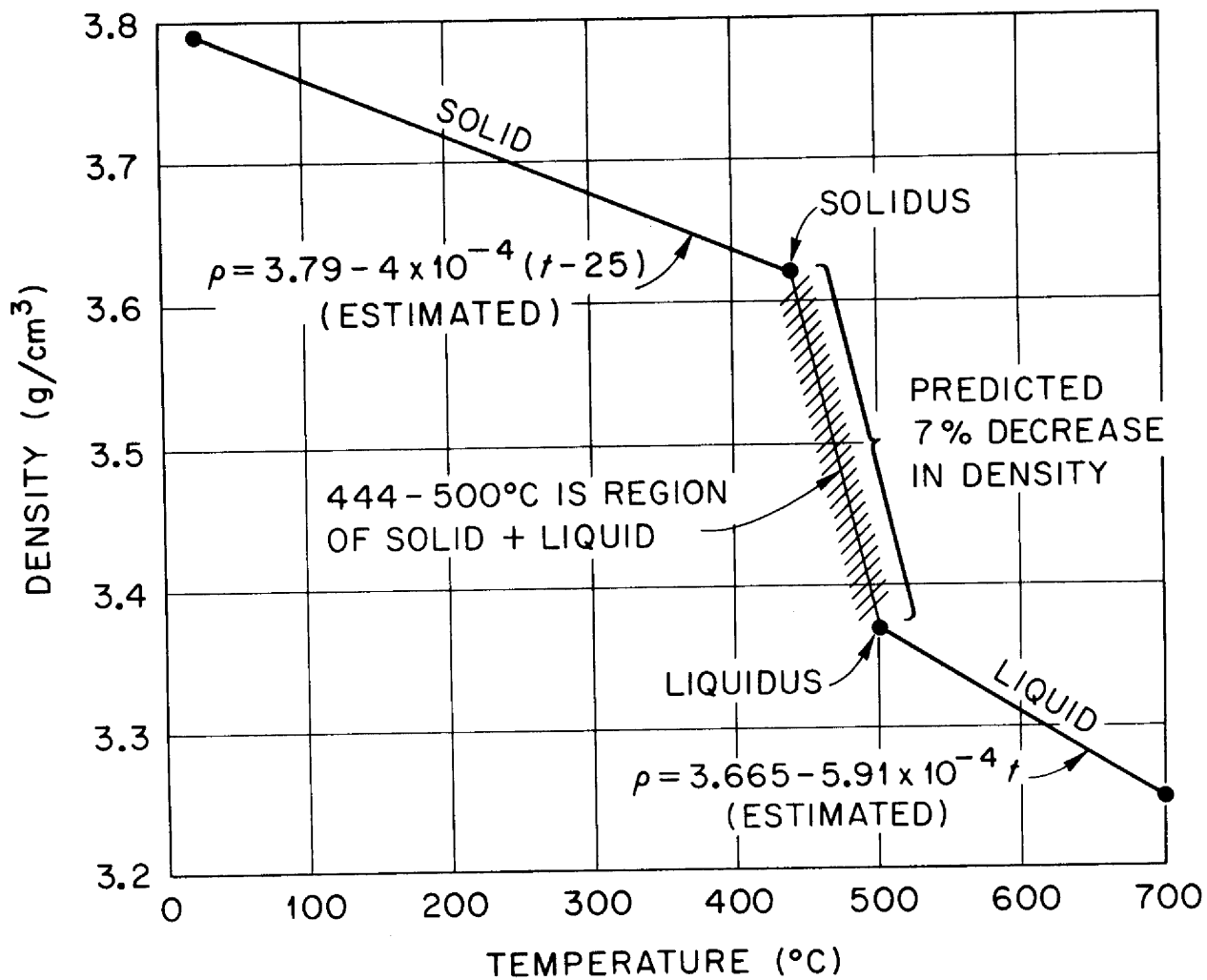
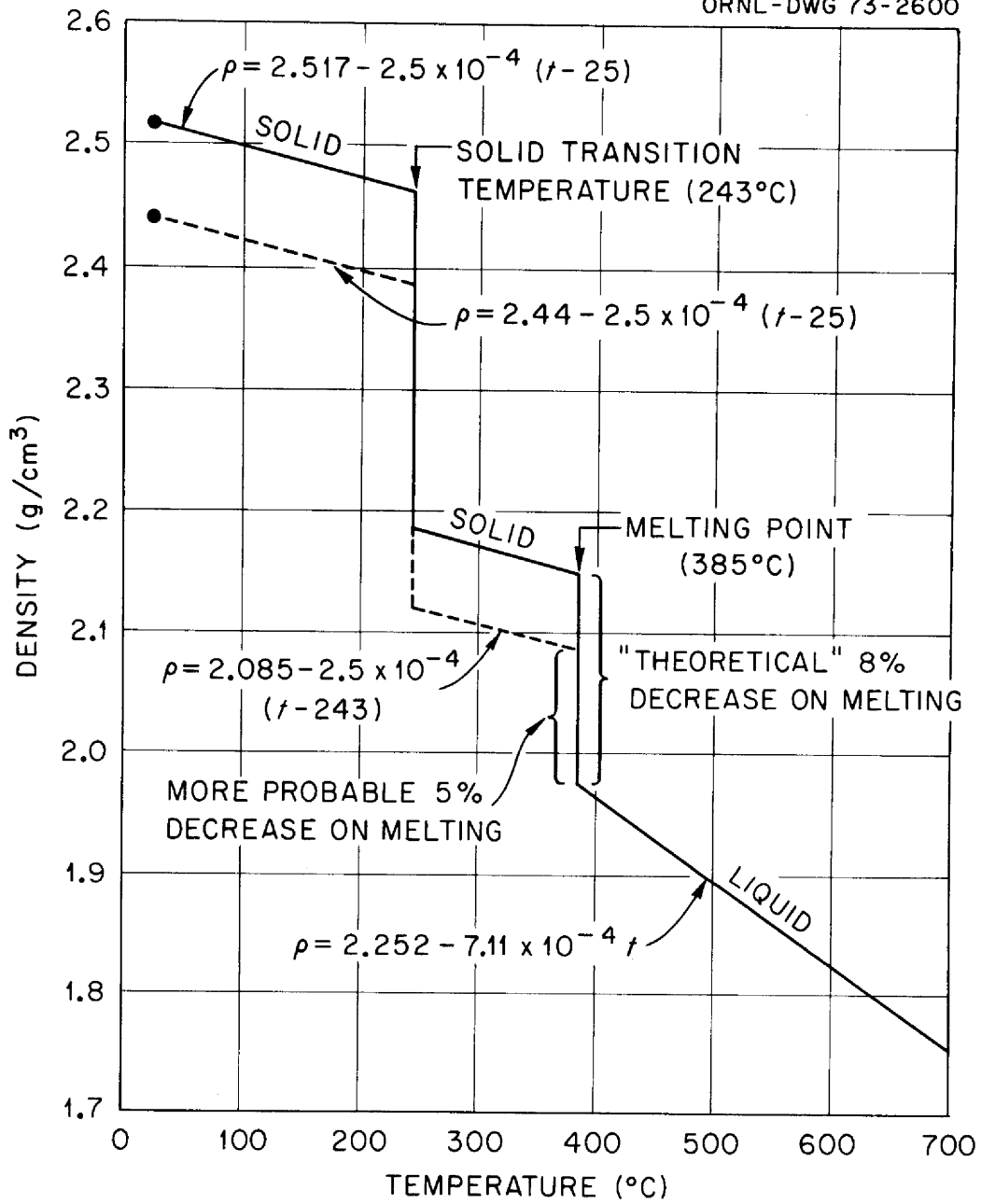


Fig. 2. Density of LiF-BeF₂-ThF₄ (72-16-12 mole %).

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Fig. 3. Density of NaBF₄-NaF (92-8 mole %).

decrease of about 5% is more likely. It should be noted that this salt undergoes a rather large density change in the solid at 243°C. The predicted density decrease at this temperature is about 12.7%.

VISCOSITY

Introduction and Experimental

Viscosity is an important physical property in assessing the heat transfer performance and fluid dynamics of reactor liquids. In these regards, information on fluoroborates was of special interest. Viscosity measurements on molten fluoroborates are relatively difficult because of their high volatility.

For volatile liquids at elevated temperatures, accurate measurement of low viscosities (<10 centipoises) are conveniently determined by oscillating-cup viscometry. In this method, a cylindrical vessel, which encapsulates the sample, is caused to execute torsional oscillations. The rate at which the amplitude of the oscillations is damped depends on the viscous drag of the liquid upon the walls of the container. The viscosity is determined through the basic equations of fluid dynamics from: the damping rate, the period of oscillation, the dimensions of the apparatus, and the mass and density of the liquid.

Over a period of several years, L. J. Wittenberg and his co-workers at Mound Laboratory, Miamisburg, Ohio (an AEC-owned facility), have gained much experience in measuring molten materials, mainly liquid metals,¹⁷ via oscillating-cup viscometry. Because it was both faster and less expensive for Mound rather than ORNL to obtain accurate viscosities of fluoroborates and other fluorides of reactor interest, a purchase order for Mound's services was obtained. Viscometric measurements and treatment of the data were performed by L. J. Wittenberg and R. Dewitt of Mound Laboratory. Preparation of samples, fabrication of capsules and supplementary interpretation of the data were done at ORNL under the supervision of the author.

The viscosities of five salt melts were determined. Two of these, single-component melts of NaBF_4 and KBF_4 , have been reported and discussed in another publication.¹⁸ The other three, the subjects of this report, are: NaBF_4 - NaF : 92-8 mole %

LiF - BeF_2 - ThF_4 : 72.7-15.7-11.6 mole % and 70.1-23.9-6.0 mole %).

Wittenberg has published details of the general technique¹⁷ and methods for treating the data.¹⁹ The specific apparatus used for this investigation is described elsewhere.¹⁸

Capsules, machined out of nickel stock, consisted of a cap and a cylindrical cup, the latter with approximate dimensions: 1.75 cm I.D., 1.85 cm O.D., and 7.5 cm long. After the dimensions were accurately measured, the capsules were charged with salt equivalent to about 15 cm³ in the expected temperature range of measurements. Weighing and charging of samples were carried out in a glovebox. After these operations, the glovebox was evacuated at $\sim 30 \mu$ for 20 hours. After flushing the box twice with helium (purified by passing through a charcoal trap maintained at liquid nitrogen temperature), the cap was fuse-welded to the cup by means of an argon arc torch. During welding, the capsule was kept in a copper block whose purpose was to absorb most of the heat generated at the weld. The efficiency of heat removal was indicated by a small piece of masking tape attached to the cup about 2.5 cm below the weld-work; the tape did not appear charred or altered by the welding operations. Success in the heat removal was confirmed by the negligible losses in capsule weights taken after welding.

Results and Discussion

The viscosities of the three salt mixtures are listed and compared with least-squares values in Tables 4, 5, and 6. The temperature of the viscosity determination was measured with a chromel-alumel thermocouple positioned near the capsule but not touching it. At each temperature, at least two, and usually three sets of amplitude and period measurements were taken; hence, there is more than one experimental viscosity entry for each temperature in Tables 4, 5, and 6. The data and least-squares fit are plotted in Figure 4.

Table 4. Viscosity of NaBF₄-NaF

(92 - 8 mole %)

Least squares fit: $\eta(\text{cP}) = 0.0877 \exp(2240/T(^{\circ}\text{K}))$

T(°C)	Experimental $\eta(\text{cP})$	Calculated $\eta(\text{cP})$
409	2.18, 2.15	2.34
411	2.15, 2.20	2.32
418	2.29, 2.29, 2.30	2.24
425	2.05, 2.05, 2.05	2.17
436	2.02, 2.00	2.06
465	1.89, 1.91, 1.86	1.82
491	1.59, 1.59, 1.59	1.64
505	1.45, 1.43, 1.47	1.56
521	1.45, 1.46	1.47
532	1.31, 1.30, 1.31	1.42
408	2.50, 2.38, 2.46 2.36, 2.38, 2.35	2.35
417	2.27, 2.35, 2.33	2.25
450	2.03, 2.04, 1.96	1.94
474	1.91, 1.96, 2.08	1.76
505	1.77	1.56
537	1.47, 1.48, 1.44	1.39

Table 5. Viscosity of LiF-BeF₂-ThF₄
(72.7-15.7-11.6 mole %)

Least-squares fit: $\eta(\text{cP}) = 0.1094 \exp(4092/T(^{\circ}\text{K}))$

T(°C)	Experimental $\eta(\text{cP})$	Calculated $\eta(\text{cP})$
553	14.1, 14.3, 14.1 ₅	15.5
582	12.4, 13.4, 13.0	13.1
613	11.4, 11.2, 11.1	11.1
638	9.74, 9.56, 9.47	9.76
622	11.5, 11.5, 11.4	10.6
588	13.4, 13.5, 13.4	12.7
555	15.5, 16.5, 16.1	15.3
572	13.4 ₅ , 13.3, 14.1 ₅	13.9
649	9.21, 9.79, 9.22	9.25
673	7.74, 7.75, 7.74	8.27

Table 6. Viscosity of $\text{LiF}-\text{BeF}_2-\text{ThF}_4$

(70.11-23.88-6.01 mole %)

Least-squares fit: $\eta(\text{cP}) = 0.06602 \exp(4380/T(^{\circ}\text{K}))$

T($^{\circ}\text{C}$)	Experimental $\eta(\text{cP})$	Calculated $\eta(\text{cP})$
653	7.30, 7.06, 7.06	7.47
547	14.1, 13.9, 14.15	13.8
598	9.87, 9.87, 9.88	10.1
633	8.92, 8.97, 8.81	8.30
526	15.39, 16.53, 16.05	15.8
567	12.35, 12.56, 12.35	12.1
579	11.06, 10.92, 10.91	11.3
603	9.69, 10.19, 9.96	9.79
557	12.59, 12.69, 11.85	12.9

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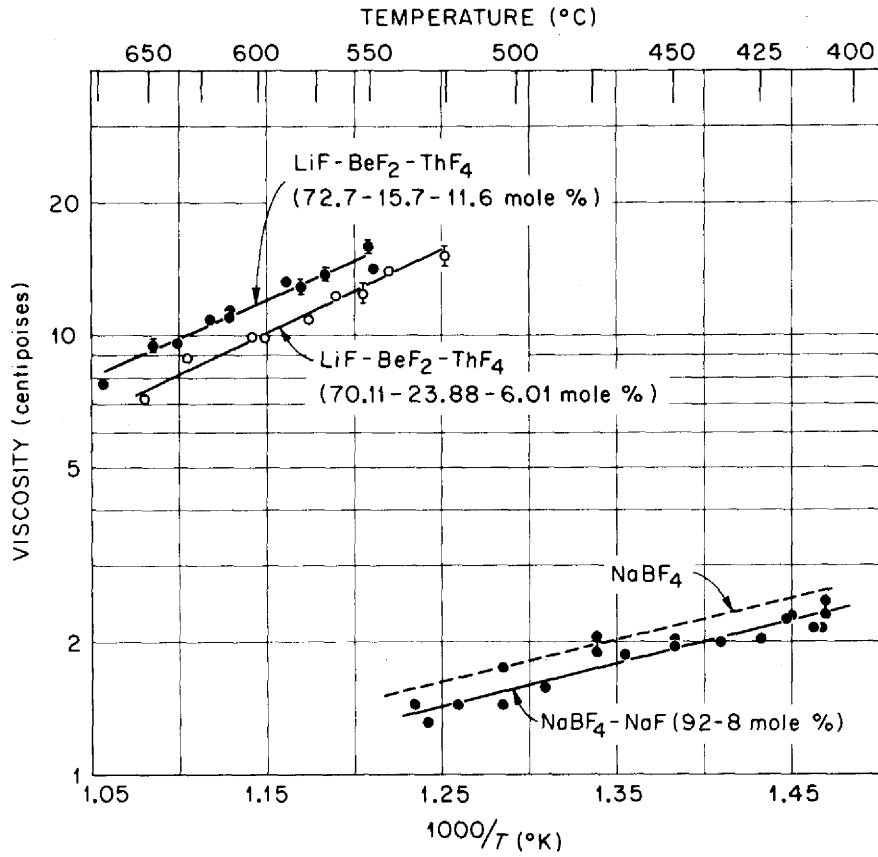


Fig. 4. Viscosities of Three Fluoride Mixtures. All the points at the bottom refer to viscosity of NaBF₄-NaF (92-8 mole %).

The viscosity of $\text{NaBF}_4\text{-NaF}$ (92-8 mole %) is very much like that of NaBF_4 .¹⁸ Evidently the presence of 8 mole % NaF leads to a somewhat lesser viscosity (see Fig. 4).

The data for the two ternary melts show that the mixture with the greater viscosity contains the lesser concentration of BeF_2 and the greater concentration of ThF_4 . Qualitatively, this behavior was predicted from the viscosity measured in mixtures of $\text{LiF-BeF}_2\text{-UF}_4$ ²⁰: "for LiF concentrations of 60 mole % or greater, substitution of UF_4 (or ThF_4) for BeF_2 (at const. temperature) causes an increase in viscosity."²¹ Indeed, as Table 7 reveals, the UF_4 -containing mixtures serve as an excellent basis for quantitatively predicting viscosities in analogous ThF_4 -containing melts.

Table 7. Viscosity at 800°K and 900°K of $\text{LiF-BeF}_2\text{-ThF}_4$ (or UF_4)

Composition (mole %)	Viscosity (cP)	
	800°K	900°K
$\text{LiF-BeF}_2\text{-ThF}_4$ 72.7-15.7-11.6	18.2	10.3
$\text{LiF-BeF}_2\text{-UF}_4$ ^a 70-18-12	18.9 ^a	10.4 ^a
$\text{LiF-BeF}_2\text{-ThF}_4$ 70.11-23.88-6.01	15.8	8.58
$\text{LiF-BeF}_2\text{-UF}_4$ ^a 70-24-6	18.5 ^a	10.1 ^a

^aSee Reference 20.

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