Liquid Density of Yttrium and Some Rare-Earth Fluorides from the Melting Points to $\cong$2500° K.

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AS PART OF an extensive program of physical-chemical measurements at high temperatures, the densities of liquid oxides (Al_2O_3) (*3*, *6*), alkaline earth fluorides (*8*, *9*), and thorium and uranium fluorides (*7*) have been measured up to 2600° K. Previously, the only data available in the literature were on mixed salts below 1000° or those reported by Jaeger (*2*) on alkali fluorides and by Mashovetz and Lundina (*10*) on calcium fluoride up to 1700°. Liquid density measurements have now been extended to include yttrium and some rare-earth fluorides, at temperatures up to 2500° K. (*4*).

EXPERIMENTAL PROCEDURE

The source of heat was the carbon tube resistance furnace in an argon atmosphere described previously (*6*). A graphite crucible (2-inch o.d. and 3 inches high, made from E821 Dixon graphite) was used for yttrium and all the rare-earth fluorides, except samarium trifluoride. The graphite crucible could not be used with SmF_3, since the graphite reduced it to SmF_2 (*5*). Therefore, a molybdenum crucible, 2⅝ inches high and 1½ inches in diameter, was used for SmF_3 (*3*). Both tungsten and molybdenum sinkers were used in these measurements.

The densities of the liquid fluorides were determined by the immersed-sinker method. The procedure consisted in measuring the weight loss of the sinker immersed in the liquid fluorides while determining simultaneously the furnace temperature by means of an optical pyrometer calibrated by measuring the melting points of platinum (2043° K.) and silver (1234.0° K.) and the boiling points of lead (2024° K.) and silver (2450° K.). Each reading was accurate to $\pm 10°$. As numerous readings were taken, however, the final temperature values had a probable standard deviation of $\pm 5°$ or $\pm 0.2\%$. The readings were made on the graphite chimney at the level of the melt and corrected for the emissivity of the graphite.

The volume, V, of the molybdenum sinker was always corrected for thermal expansion to the operating temperature, T, using the best values selected by Bockris, White, and Mackenzie (*1*) for the thermal coefficient of expansion of molybdenum. The density of the melt was calculated from the equation

$$D = \frac{W_A - W_M}{V_T}$$

where W_A and W_M are the weights of the sinker in air and in the melt, respectively. The value obtained from the above equation was always corrected for the buoyancy in air. This correction was never more than +0.0005 gram per cc. The density value was also corrected for the effect of surface tension. This correction was never more than 0.5%.

MATERIALS USED

The fluorides, obtained from Lindsay Chemical Division, had a purity of 99.9 to 99.99%. They were predried by heating slowly first to 100° C. and finally to 300° C. while evacuating to less than 1 mm. of Hg. This procedure was followed to prevent the reaction of the fluorides with water at high temperatures with the formation of the oxide and HF.

Since it is difficult to remove all the water, samples of the fluorides after use were analyzed for oxides. At no time was there more than 0.3% oxide, which necessitated a correction of less than 3 parts per thousand. After each run, the fluorides were also analyzed for total carbon and carbide when graphite crucibles were used and for molybdenum in any form when molybdenum crucibles were used. The maximum amounts of impurities found were $<0.1\%$ carbon, $<0.1\%$ carbide, and $<0.01\%$ molybdenum. The impurities required a maximum correction of 0.02%.

RESULTS

The liquid densities of yttrium, praseodymium, and samarium trifluorides were determined over a temperature range of 1700° to 2400° K. The values have straight-line relationships when density is plotted against temperature, as shown in Figure 1. The equations of these straight lines are given in Table I, with those reported previously for lanthanum and cerium trifluorides (*9*). The probable average deviation between the experimental densities and those calculated from the equations are ± 0.004 gram per cc. for YF_3, ± 0.007 for PrF_3, and ± 0.005 for SmF_3.

Table I. Liquid Density Equations of Yttrium and Rare-Earth Fluorides

Fluoride	Temp. Range, ° K.	Density Equation, G./Cc.
YF_3	1700–2100	$D = 4.661 - 5.14 \times 10^{-4}\ T^{\circ}$ K.
LaF_3	1750–2450	$D = 5.793 - 6.82 \times 10^{-4}\ T^{\circ}$ K.
CeF_3	1700–2200	$D = 6.253 - 9.36 \times 10^{-4}\ T^{\circ}$ K.
PrF_3	1880–2300	$D = 6.012 - 7.00 \times 10^{-4}\ T^{\circ}$ K.
SmF_3	1780–2300	$D = 5.805 - 5.55 \times 10^{-4}\ T^{\circ}$ K.

Extrapolation of the equations in Table I gives the following densities at the melting points (*11*) and boiling points (*11*) of the rare earth fluorides:

	$D_{\text{m.p.}}$, G./Cc.	$D_{\text{b.p.}}$, G./Cc.
YF_3	3.808 (1660° K.)	3.376 (2500° K.)
LaF_3	4.634 (1700° K.)	4.020 (2600° K.)
CeF_3	4.631 (1733° K.)	3.819 (2600° K.)
PrF_3	4.862 (1643° K.)	4.192 (2600° K.)
SmF_3	4.879 (1670° K.)	4.362 (2600° K.)

Using the smoothed-density values obtained from these density equations, the molar volumes for the liquid fluorides were calculated and are summarized in Table II.

It was previously (*9*) shown that the molar volumes of the liquid fluorides of the metals of Periods 4, 5, and 6 are the same when $T/T_{\text{b.p.}=0.75}$ whether they are in Group IA, IIA, or IIIA. For example, the molar volumes of CsF, BaF_2, LaF_3, and CeF_3 were 44.45 ± 0.45 and those of RbF and SrF_2 were 38.81 ± 0.06 cc. per mole. Since YF_3 is a

Table II. Liquid Molar Volumes of Yttrium and Rare-Earth Fluorides

	YF_3		LaF_3		CeF_3		PrF_3		SmF_3	
Temp., ° K.	Density, g./cc.	Molar vol., cc./mole	Density, g./cc.	Molar vol., cc./mole	Density, g./cc.	Molar vol., cc./mole	Density, g./cc.	Molar vol., cc./mole	Density, g./cc.	Molar vol., cc./mole
1700	3.788	38.53	...	...	4.662	42.29	...	...	4.862	42.66
1800	3.736	39.06	4.565	42.92	4.568	43.15	...	...	4.807	43.15
1900	3.685	39.60	4.497	43.57	4.475	44.05	4.682	42.27	4.751	43.66
2000	3.633	40.16	4.429	44.24	4.381	45.00	4.612	42.91	4.696	44.17
2100	3.582	40.74	4.360	44.93	4.288	45.98	4.542	43.58	4.640	44.70
2200	...	...	4.292	45.65	4.194	47.00	4.472	44.26	4.585	45.24
2300	...	...	4.224	46.38	...	...	4.402	44.96	4.529	45.80
2400	...	...	4.156	47.14	...	...	...	...	...	...

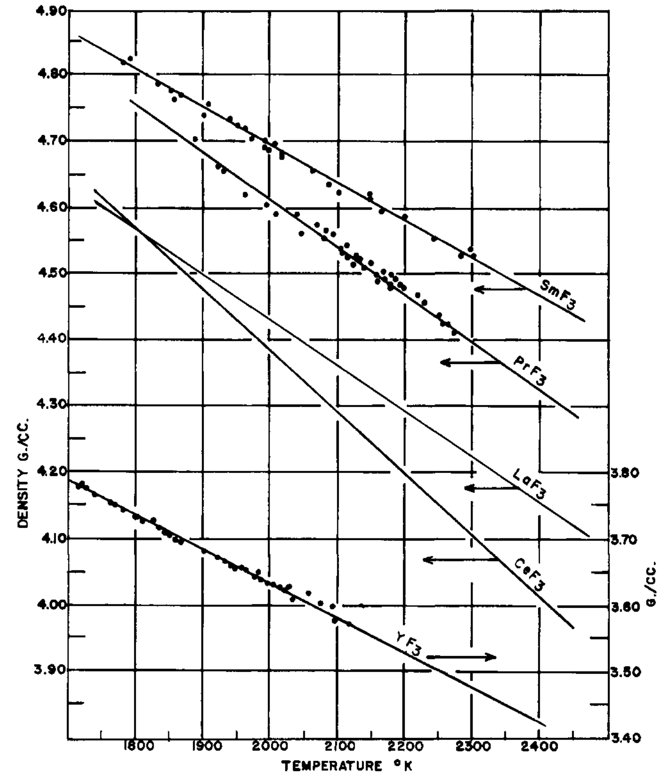

Figure 1. Liquid densities of yttrium and rare-earth fluorides

compound of a metal in the same period as Rb and Sr, it was assumed that its molar volume would also be 38.8. Thus, at 1875° K., its density should be 3.76 grams per cc. The experimental equation given above shows that the density of YF_3 at 1875° K. is equal to 3.70 grams per cc.

The relationship between volume, V, and cubical coefficient of expansion, β, is

$$V_t = V_i(1 + \beta\Delta t)$$

where i and t are the initial and final temperatures.

Since

$$\frac{V_t}{V_i} = \frac{D_i}{D_t}$$

the equation becomes:

$$D_i = D_t(1 + \beta\Delta t)$$

or

$$\Delta D/\Delta t = \beta(D_t)$$

where D is the density of the liquid fluoride.

Using the above equation, the cubical coefficients of expansion of the rare-earth fluorides in the liquid state were calculated for various temperatures. They are tabulated in Table III.

Table III. Cubical Thermal Coefficient of Expansion

	Cubical Expansion Coefficient, $\beta \times 10^6$ (T^{-1})				
Temp., ° K.	YF_3	LaF_3	Cef_3	PrF_3	SmF_3
1700	135.7	...	200.8	...	114.2
1800	137.5	149.4	204.9	...	115.4
1900	139.4	151.7	209.2	149.5	116.8
2000	141.4	154.0	213.6	151.8	118.1
2100	143.4	156.4	218.3	154.1	119.5
2200	...	158.9	223.2	156.5	121.0
2300	...	161.5	...	159.0	122.5
2400	...	164.1	...	...	...

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