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VAPOR PRESSURE AND HEAT OF SUBLIMATION
OF CERIU(III) FLUORIDE

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OF CERIUM(III) FLUORIDE

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May 20, 1965

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OF CERIUM(III) FLUORIDE

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ABSTRACT

The vapor pressure of CeF_3 was measured in the temperature range 1370°K to 1685°K by the torsion-effusion method. The vapor pressure of CeF_3 in atmospheres is given in the experimental range by the expression

$$\log_{10} P = - (1.983 \pm 0.013) \times \frac{10^4}{T} + 8.816 \pm 0.086 ,$$

where the quoted errors are the standard deviation from the least-squares fit. Extrapolations yield a calculated normal boiling point of 2472°K and a heat of sublimation at 298.15°K of 99.51 ± 0.25 kcal/mole by the third-law method and 99.29 ± 0.58 kcal/mole by the second-law method.

I. INTRODUCTION

The science and technology of rare earth elements and compounds has been given increasing significance in recent years. Although a great deal of advancement has been made in this field, available thermodynamic data for rare earth compounds are still few in number. No quantitative vapor pressure data have been obtained for fluorides of rare earth compounds.

This paper reports the result of measurements of the vapor pressure of cerium(III) fluoride by the torsion-effusion method.^{1,2} Among other applications, cerium(III) fluoride is used as ion-source material, laser host, and an important intermediate compound in the production of cerium metal.

II. EXPERIMENTAL

In the torsion-effusion method an effusion cell was suspended in a vacuum furnace by a fine wire. As the system is heated, vapor effuses from two eccentrically placed orifices in the cell exerting a torsional force on the wire. The angle through which the cell is turned is measured, and from this angle the vapor pressure can be calculated by means of the expression

$$P = \frac{2\phi D}{\sum qaf},$$

where P is the vapor pressure of the material in the cell, ϕ is the angle through which the cell has rotated, D is the torsion constant of the suspension wire, q is the distance from the orifice to the axis of rotation of the cell, a is the area of the orifice, and f is the correction factor for the finite channel length of the orifice.³⁻⁵

For this research, the suspension wire was 0.0127 cm wide, 0.00254 cm thick, and 45 cm long tungsten ribbon. Components of the effusion cell and cell block were made of National Carbon ZT101 grade graphite. Two parallel holes of 1.3 cm diam with axis 1.35 cm from the center of the cell block were drilled through the block, and two loaded effusion cells with effusion orifices oriented to yield additive torques were fitted into these holes. Three different orifice dimensions were used as shown in Table I.

The cerium(III) fluoride sample, prepared by the reduction of ceric oxide by anhydrous hydrogen fluoride at 850°C, was supplied by Semi-Elements, Inc. To establish that the observed steady-state pressures

Table I. Orifice dimensions.*

Cell	Hole diameter (cm)		Lid thickness (cm)		Channel factor	
	(1)	(2)	(1)	(2)	(1)	(2)
1	0.07790	0.08125	0.09931	0.10389	0.51240	0.51175
2	0.13842	0.12412	0.10516	0.10211	0.63962	0.62058
3	0.25182	0.25284	0.10261	0.10236	0.77282	0.77396

*The torsion constant for these runs was $1.76 \text{ dyn-cm-rad}^{-1}$. The moment arm was 1.35 cm.

were not produced by vaporization of salts of metals present as impurities, a sample was placed in a graphite cell and heated in an induction furnace at about 1650°K at pressures below 5×10^{-5} torr until about two-thirds of the loaded sample had sublimed. Then a glass disk was placed near the cell block, and vapor was allowed to condense on the disk for about 2 hr at 1600°K. This condensed material, the residual material in the cell, and a sample of the untreated cerium(III) fluoride were spectrographically analyzed by the American Spectrographic Laboratories. The results are given in Table II. The only major impurity reported for the sublimate, silicon, presumably was a contaminant from the collection disk since the silicon content of the original sample was below the limit of detection.

Temperatures were measured with an optical pyrometer. A black-body hole was drilled at the bottom of the cell block. During temperature measurement, this hole could not be seen except immediately after the cell temperature was changed. This fact indicates that black-body conditions prevailed and that the cell block was very uniform in temperature.

In a typical run, about 1 g of cerium(III) fluoride was loaded into each of the two effusion cells. Covers were placed over the apertures in the cells, and the cells were then fitted into the holes in the cell block. The power was raised slowly enough to keep the ambient pressure below 5×10^{-5} torr until 1650°K was reached. This process took about 5 hr when new samples were loaded. The cell was allowed to remain at this temperature for about an hour before deflection and temperature data were taken. However, if samples already used in a previous

Table II. Spectrographic analysis of CeF_3 samples.^a

Element	Original sample ^b	Sublimate ^c	Residue in cell ^d
Ce	Principal constituent in all three samples		
Si	--	6. %	--
Fe	0.15%	0.05	--
Mg	0.75	1.25	0.003%
Mn	--	0.001(?)	--
Pb	0.004	--	--
Sn	0.04	--	--
Al	0.015	--	--
Gd	1.	0.07	0.3
Cu	--	0.001	--
Na	0.2	--	--
Ti	0.005	--	--
La	1.75	1.75	2.
Zr	0.02	<0.01	<0.01
Ca	Not determinable, Ce interference		
Ba	--	0.003(?)	--
Cr	0.003	0.004	--
Nd	1.5	1.25	1.5
Pr	0.25	0.2	0.3
Sm	0.1(?)	0.1(?)	0.1(?)

^aReported on oxide-basis of the elements indicated.

^bPrepared by reduction of ceric oxide by anhydrous hydrogen fluoride at 850°K; supplied by Semi-Elements, Inc.

^cSublimating vapor was condensed on a glass disk in an induction furnace at about 1600°K; about two-thirds of the loaded sample was sublimated before sample collection to match the actual experimental condition.

^dResidual samples in cell after sublimates had been collected.

run and kept in the system under vacuum were reheated, it took about 20 min to heat to 1650°K and required only about 15 min at this temperature before measurements were begun.

The original sample may have been partially hydrated. Staritzky and Asprey⁶ and Batsanova et al.⁷ have demonstrated that heating hydrated rare earth fluorides in a vacuum at temperatures of 1273 to 1573°K for an hour results in anhydrous fluorides. In our experiment, after about 1300°K was reached, a much faster power increase was possible with the pressure still held below 5×10^{-5} torr, possibly because dehydration was completed below 1300°K.

The original fine granular sample was sintered after heating to about 1300°K and became orange-brown in color. Heating for longer periods of time at 1600°K made the sample optically anisotropic. Staritzky et al.⁶ and Batsanova et al.⁷ have previously observed the development of optical anisotropy for rare earth metal fluorides after heating a long time at high temperatures. They explained the phenomenon as a result of a decrease in defects in the crystal and an increase in ordering of the hexagonal crystal structure. Batsanova et al.⁷ also showed that during heating at 1273 to 1573°K neither changes in crystal structure nor significant changes in chemical composition in rare earth metal halides occur. The sample after degassing was anhydrous cerium fluoride containing approximately $3 \pm 1\%$ of impurities of partial pressures comparable with the pressure of the cerium fluoride. These impurities were almost certainly in solution in the cerium fluoride and should reduce the partial pressure of cerium fluoride by about 3%. Since this

pressure reduction should be approximately equal to the partial pressures of the impurities, no correction was made to the measured pressures.

The temperature was either lowered or raised successively in steps of 5 to 15°K and allowed to equilibrate at each temperature for about 15 min before deflection and temperature readings were taken. Some of the data were obtained by varying temperatures randomly. The zero-point deflection position was recorded at room temperature for each run of experiment. These pressures are shown in Table III and Fig. 1.

A more detailed description of the apparatus and techniques is given elsewhere.⁸

Table III. Temperature, pressure, ratios of mean free path to orifice diameter, and the third-law heat of sublimation of CeF_3 .

Temp (°K)	Pressure (atm)	λ/d	ΔH_{298}° (kcal/mole)
1653	7.655×10^{-4}	0.15	98.88*
1662	8.731×10^{-4}	0.14	98.95*
1651	7.716×10^{-4}	0.15	98.75*
1644	6.786×10^{-4}	0.17	98.78*
1641	6.185×10^{-4}	0.19	98.92*
1663	8.549×10^{-4}	0.14	99.05*
1656	7.216×10^{-4}	0.16	99.26*
1642	5.871×10^{-4}	0.20	99.15*
1683	1.316×10^{-3}	0.09	98.70*
1675	1.100×10^{-3}	0.11	98.85*
1685	1.223×10^{-3}	0.10	99.02*
1682	1.099×10^{-3}	0.11	99.24*
1676	9.555×10^{-4}	0.12	99.46*
1667	8.236×10^{-4}	0.14	99.41*
1548	8.792×10^{-5}	1.25	99.87*
1560	1.187×10^{-4}	0.94	99.66*
1631	4.143×10^{-4}	0.28	99.70*
1622	3.719×10^{-4}	0.31	99.55*
1532	7.364×10^{-5}	0.90	99.51
1543	9.393×10^{-5}	0.71	99.34
1559	1.235×10^{-4}	0.54	99.48
1571	1.443×10^{-4}	0.47	99.67
1577	1.638×10^{-4}	0.42	99.63
1579	1.849×10^{-4}	0.37	99.35
1536	8.356×10^{-5}	0.79	99.34
1543	9.423×10^{-5}	0.71	99.38
1552	1.078×10^{-4}	0.62	99.49
1556	1.201×10^{-4}	0.56	99.40
1566	1.384×10^{-4}	0.49	99.52
1572	1.548×10^{-4}	0.43	99.48
1576	1.751×10^{-4}	0.39	99.35
1587	2.038×10^{-4}	0.34	99.50
1592	2.453×10^{-4}	0.28	99.20
1600	2.891×10^{-4}	0.24	99.14
1605	3.243×10^{-4}	0.21	99.04
1604	3.057×10^{-4}	0.27	99.17
1600	2.672×10^{-4}	0.26	99.39
1592	2.746×10^{-4}	0.25	99.84
1597	2.609×10^{-4}	0.26	99.30
1592	2.325×10^{-4}	0.30	99.37

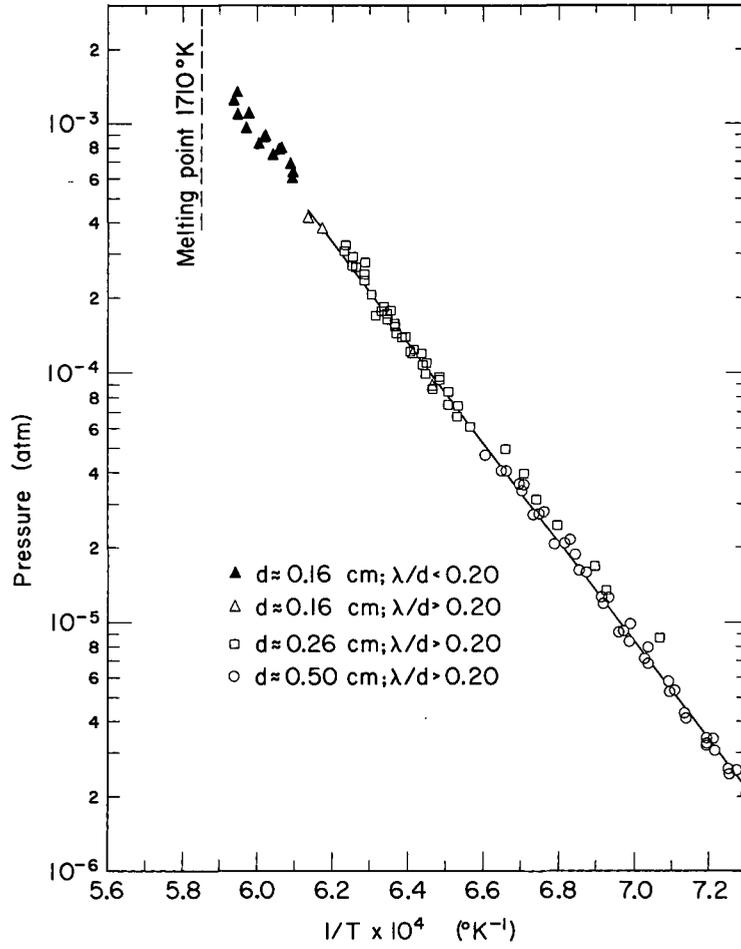
Table III. (cont.)

Temp (° K)	Pressure (atm)	λ/d	ΔH_{298}° (kcal/mole)
1580	1.811×10^{-4}	0.38	99.48
1587	1.737×10^{-4}	0.39	99.50
1578	1.668×10^{-4}	0.41	99.63
1573	1.506×10^{-4}	0.45	99.66
1568	1.374×10^{-4}	0.49	99.67
1562	1.222×10^{-4}	0.55	99.66
1557	1.093×10^{-4}	0.61	99.73
1552	9.814×10^{-5}	0.68	99.78
1547	8.611×10^{-5}	0.77	99.88
1539	7.364×10^{-5}	0.89	99.90
1525	6.041×10^{-5}	1.07	99.68
1502	4.974×10^{-5}	1.29	98.91
1489	3.952×10^{-5}	1.62	98.82
1483	3.126×10^{-5}	2.04	99.15
1471	2.450×10^{-5}	2.59	99.16
1450	1.698×10^{-5}	3.68	98.94
1444	1.353×10^{-5}	4.61	99.23
1415	8.716×10^{-6}	6.99	98.66
1491	3.598×10^{-5}	0.93	99.22
1479	2.783×10^{-5}	1.19	99.25
1465	2.127×10^{-5}	1.55	99.21
1455	1.584×10^{-5}	2.07	99.44
1442	1.258×10^{-5}	2.12	99.31
1431	9.886×10^{-6}	3.24	99.32
1421	7.989×10^{-6}	3.82	99.28
1411	5.792×10^{-6}	5.40	99.57
1403	4.327×10^{-6}	7.20	99.86
1387	3.428×10^{-6}	9.09	99.44
1374	2.563×10^{-6}	12.06	99.37
1370	2.064×10^{-6}	14.92	99.70
1380	2.596×10^{-6}	11.95	99.74
1390	3.428×10^{-6}	9.12	99.65
1390	3.229×10^{-6}	9.68	99.81
1407	5.292×10^{-6}	5.98	99.53
1432	8.288×10^{-6}	3.89	99.88
1446	1.192×10^{-5}	2.73	99.72
1462	1.871×10^{-5}	1.76	99.39
1481	2.719×10^{-5}	1.23	99.46
1502	4.014×10^{-5}	0.84	99.55
1390	3.295×10^{-6}	9.49	99.75
1421	6.824×10^{-6}	4.68	99.74
1447	1.272×10^{-5}	2.56	99.59

Table III. (cont.)

Temp (° K)	Pressure (atm)	λ/d	ΔH_{293}° (kcal/mole)
1468	2.074×10^{-5}	1.59	99.46
1492	3.388×10^{-5}	0.99	99.45
1514	4.673×10^{-5}	0.73	99.79
1504	4.064×10^{-5}	0.83	99.63
1493	3.585×10^{-5}	0.94	99.35
1485	2.706×10^{-5}	1.32	99.71
1474	2.070×10^{-5}	1.60	99.81
1459	1.601×10^{-5}	2.05	99.66
1446	1.195×10^{-5}	2.72	99.71
1436	9.253×10^{-6}	3.49	99.82
1423	7.223×10^{-6}	4.43	99.70
1411	5.259×10^{-6}	6.04	99.82
1402	4.194×10^{-6}	7.52	99.87
1386	3.096×10^{-6}	10.07	99.67
1378	2.496×10^{-6}	12.42	99.72
1370	2.097×10^{-6}	14.70	99.66

*Indicates heats for which calculated λ/d was smaller than 0.20. The first 18 points, the next 40 points, and the last 40 points were taken with the sets of small, medium, and the large orifices, respectively.



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Fig. 1

III. RESULTS AND DISCUSSION

Studies⁹⁻¹¹ on low pressure gas flow have demonstrated that the molecular flow equations become inapplicable when the ratio of the mean free path of the vapor, λ , to the diameter of the effusion orifice, d , exceeds a certain value for a given orifice. At lower λ/d the measured pressures deviate upward from the equilibrium vapor pressure, and heats calculated by the third-law method are smaller than the true heat of sublimation. Table III shows for each measurement the calculated ratios λ/d in addition to the pressure and the third-law values of the heat of sublimation at 298°K. The ratio λ/d is calculated by using the hard sphere approximation¹² with the molecular diameter of cerium(III) fluoride taken as 7.36Å, the sum of ionic diameters at room temperature, assuming the molecule to form a planar triangle. The numerical values calculated by this approximation has significance only for internal comparison. In the final calculation of ΔH_{298}° , data for which the ratio λ/d is smaller than 0.2 are excluded. The choice of this value was somewhat arbitrary.

In Fig. 1 closed triangles indicate those points with calculated λ/d ratios less than 0.2; open triangles, squares, and circles indicate points with ratios greater than 0.2. The solid line is given by a least-squares fit of the vapor pressures of cerium(III) fluoride for those data with λ/d ratios larger than 0.2. This line can be expressed in atmospheres as

$$\log_{10} P = - (1.983 \pm 0.013) \times \frac{10^4}{T} + 8.816 \pm 0.086 .$$

The errors are the standard deviations from the least-squares fit.

For each orifice diameter the heat of sublimation of cerium(III) fluoride at 298°K is calculated by both the second-law (sigma plot) method and the third-law method. For the second-law method the equation

$$\frac{\Delta H_I^\circ}{T} + I = \sum = -R \ln P + \Delta a \ln T + 1/2 \Delta b T + 1/2 \Delta c T^{-2}$$

was used, where ΔH_I° and I are constants from which the heat and entropies of sublimation can be calculated, and a, b, and c are the constants in the heat capacity equation $C_p = a + bT + cT^{-2}$.

For $\text{CeF}_3(\text{s})$ King and Christensen¹³ report that $C_p = 17.90 + 10.14 \times 10^{-3} T + 1.10 \times 10^5 T^{-2}$ in the range from 298° to 1799°K.

Only $\text{CeF}_3(\text{g})$ is believed to be a significant vapor species. Brewer¹⁴ showed that dimers of trihalides in vapor species are found only for trihalides with low boiling points and with cation-to-anion radius ratios lying in a narrow range. Cerium(III) fluoride has a relatively high boiling point and the cation-to-anion radius ratio is by far the larger than this range, so sublimation as polymers is very unlikely. Thermodynamic calculations show that the partial pressures of $\text{CeF}(\text{g})$, $\text{CeF}_2(\text{g})$, and $\text{CeF}_4(\text{g})$ which may be produced by various disproportionation and decomposition reactions are at least several orders of magnitude smaller than the observed pressures; also, the pressures of $\text{CF}_4(\text{g})$, $\text{C}_2\text{F}_6(\text{g})$, $\text{C}_2\text{F}_4(\text{g})$, $\text{Ce}(\text{g})$, and $\text{F}_2(\text{g})$ which may be produced by the reaction of the sample with the graphite cell are all several orders of magnitude below the observed pressures.

In order to calculate heat capacities and free energy functions for $\text{CeF}_3(\text{g})$, molecular constants were estimated. Batsanova et al.⁷

observed strong absorption spectra of 410 cm^{-1} in crystalline CeF_3 and identified this vibration as valence vibration of the Ce-F bond. In AlF_3 crystal, the observed Al-F valence vibrational frequency was 615 cm^{-1} , while for AlF_3 gas molecule the calculated stretching vibrational frequency was reported to be 640 cm^{-1} .¹⁵ The molecular shape of $\text{CeF}_3(\text{g})$ is assumed to be the same as $\text{AlF}_3(\text{g})$, i. e., planar triangular molecule belonging to D_{3h} point group. The estimation of the symmetrical stretching vibrational frequency¹⁶ of $\text{CeF}_3(\text{g})$ is made from the valence vibrational frequency of $\text{CeF}_3(\text{s})$ by multiplying the ratio of these two frequencies in AlF_3 . This gives a frequency of 427 cm^{-1} , from which the stretching force constant is calculated to be $2.04 \times 10^5 \text{ dyn/cm}$. This result is checked by a calculation that makes use of an empirical relationship reported by Herschbach and Laurie.¹⁷

They find for the quadratic force constant k_1 the relationship

$$k_1 = 10^{-(r_e - a_{ij})/b_{ij}},$$

where r_e is the bond distance, a_{ij} and b_{ij} are empirically determined constants that depend on the rows in the periodic table to which the atoms of the molecule belong. From a_{ij} and b_{ij} values given by Herschbach et al.,¹⁷ the unknown a_{ij} and b_{ij} values for cerium(III) fluoride were estimated to be 2.24 and 0.57, respectively. The bond distance was estimated by means of the expression $R_I/R_{II} = (B_{I,II}/B_{II,I})^{1/(n-1)}$ given by Pauling,¹⁸ where R is the interionic distance, B is repulsive coefficient, A is madelung constant, n is Born exponent factor, and subscripts I and II refer to two different crystal structures with different coordination numbers. As a first

approximation, this expression was directly applied for crystal and gas molecules of CeF_3 . For AlF_3 from known bond distances and estimated value of $n = 7.1$, $(B_{\text{I} \text{A}_{\text{II}}}/B_{\text{II} \text{A}_{\text{I}}}) = 1.89$ was obtained. With this and $n = 6.46$ which is the observed value for CsF ,¹⁸ the Ce-F bond distance of 2.09\AA for $\text{CeF}_3(\text{g})$ was obtained. The force constant calculated from the Herschbach expression is 1.83×10^5 dyn/cm, which agrees with the value from the former approximation to within 10%.

To obtain frequencies of other vibrational modes of $\text{CeF}_3(\text{g})$, $k_1 = 2.04 \times 10^{-5}$ was used to obtain out-of-plane and in-plane bending force constants,¹⁶ k_{Δ}/l^2 and k_{δ}/l^2 , respectively. A semilogarithmic plot of these two bending force constants vs stretching force constants for several known molecules^{15,16} of point group D_{3h} gave approximate straight lines. By extrapolation to the assumed stretching force constant of $\text{CeF}_3(\text{g})$, $k_{\Delta}/l^2 = 0.20 \times 10^5$ and $k_{\delta}/l^2 = 0.105 \times 10^5$ were obtained. Valence-force model calculation then yielded for vibrational frequencies of $\text{CeF}_3(\text{g})$ 427, 159, 470(2), and 181(2) cm^{-1} .

For the calculation of the electronic contribution to the heat capacity, Ce^{+3} electronic energy levels were used, thus neglecting the perturbation effect of fluorine ions. Brewer et al.¹⁹ showed that this approximation yielded good results for thermodynamic calculations when applied to dihalides of transition metals. The ground state of Ce^{+3} is $^2F_{5/2}$.²⁰ The first excited level is $^2F_{7/2}$ at 2253 cm^{-1} .²⁰ Contributions from higher levels are insignificant for the temperature range of this work.

The results of the calculated heat capacities for $\text{CeF}_3(\text{g})$ are given in Table IV from 100° to 1800°K at 100° intervals. For the temperature

Table IV. Calculated heat capacities for gaseous cerium(III) fluoride.

Temp, °K	C_p , cal/deg/mole	Temp, °K	C_p , cal/deg/mole
100	11.956	1000	20.612
200	15.805	1100	20.726
298.15	17.630	1200	20.794
300	17.649	1300	20.830
400	18.565	1400	20.841
500	19.132	1500	20.835
600	19.566	1600	20.808
700	19.929	1710	20.784
800	20.211	1800	20.746
900	20.448		

range from 300°K to 1800°K, these heat capacities may be expressed by

$$C_p = 20.214 + 0.477 \times 10^{-3} T - 2.629 \times 10^{-5} T^{-2}.$$

The least-squares calculation yields $\sum = (97.782 \pm 0.585) \times 10^3/T - 35.473 \pm 0.392$, from which the second-law value of $\Delta H_{298}^\circ = 99.29 \pm 0.58$ kcal/mole was obtained.

For the third-law calculation, enthalpy and entropy data were available for solid CeF_2 at 100° intervals.¹³ Westrum and Beale²¹ gave 27.54 eu/mole as the entropy of $CeF_3(s)$ at 298.15°K, in good agreement with 27.6 ± 0.2 eu/mole given by King and Christensen.¹³ For the calculation of free energy functions of gaseous CeF_3 , the vibrational frequencies estimated above and Ce^{+3} electronic levels are used. The rotational partition function was calculated from the estimated bond distance for $CeF_3(g)$. Calculated free energy functions for $CeF_3(g)$ are listed in Table V.

The free energy functions for condensed and gas phases together with the individual pressure values in the equation

$$\Delta H_{298}^\circ = -RT \ln P_T - T \left(\frac{\Delta F_T^\circ - \Delta H_{298}^\circ}{T} \right)$$

gave third-law values at 298°K. The pressure data show slight systematic displacements at the temperature at which the pyrometer scales are changed, about 1500°K. This effect may be due to systematic error in temperature readings with one or both temperature scale-ranges of the pyrometer. The pyrometer was recalibrated very recently by the D.C. Standards Laboratory, Lawrence Radiation Laboratory. The average third-law ΔH_{298}° value with standard deviations from the 47 vapor pressure

Table V. Calculated free energy functions for gaseous cerium(III) fluoride.

Temp (°K)	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$ (cal/deg/mole)
298.15	77.966
500	80.023
1000	87.561
1300	91.377
1400	92.647
1500	93.643
1600	94.670
1710	95.778
1800	96.599

points measured below 1515°K, 37 points between 1515 and 1631°K, and total 84 points between 1370 and 1631°K are 99.50 ± 0.28 , 99.52 ± 0.21 , and 99.51 ± 0.25 kcal/mole, respectively. The differences among these three average values all lie well within the quoted standard deviation. The highest temperature range 14 data for which λ/d were calculated to be smaller than 0.2 were more scattered because the swing of the torsion system was relatively irregular at these pressures. Although these measurements were not included in final calculation, the third-law value calculated from these data, 99.03 ± 0.79 kcal/mole, gives no indication of significant break from molecular flow.

Assuming a maximum of $\pm 2\%$ error from the effect of impurities and an additional $\pm 10\%$ error in pressure reading for uncertainties in measuring orifice areas, lid thickness, moment arms, torsion constants, and deflection angles, the total pressure error would not exceed $\pm 0.4\%$ error in ΔH_{298}° values.

The maximum probable error in temperatures, principally from uncertainties in calibrating and reading the pyrometer, is $\pm 10^{\circ}$ which would yield $\pm 0.6\%$ error in ΔH_{298}° values. The uncertainty in ΔH_{298}° resulting from the experimental measurements is thus ± 1 kcal/mole. The principal source of errors in the free energy functions should be that arising from estimations for gaseous cerium(III) fluoride. An error of $\pm 15\%$ in vibrational frequencies and an error of $\pm 0.1 \text{ \AA}$ in bond distance will give $\pm 1.5\%$ and $\pm 0.2\%$ errors in free energy functions, respectively. Taking into account other sources of errors, the calculated free energy functions may be uncertain by about $\pm 2\%$. Considering all these estimated errors, the third-law heat of sublimation should be correct to within ± 3 kcal/mole.

The melting point,^{13,22-24} heat of fusion, and liquid heat capacity of cerium(III) fluoride were reported to be 1710°K,²⁴ 13.20 kcal/mole,¹³ and 32.00 cal/deg/mole,¹³ respectively. Combining these values with the second-law equation of this work, the vapor pressure in the liquid range may be expressed as

$$\begin{aligned} -R \ln P = & (93.93 \pm 0.58) \times 10^3/T - 129.55 \pm 1.07 \\ & + 11.79 \ln T - 0.24 \times 10^{-3} T + 1.32 \times 10^5 T^{-2} \end{aligned}$$

where quoted errors are the standard deviations. From this expression, the normal boiling point of $2472 \pm 77^\circ\text{K}$ and the heat and entropy of vaporization, 66.36 ± 0.58 kcal/mole and 26.85 ± 0.23 eu/mole, at the normal boiling point were obtained. Brewer¹⁴ estimated for these values 2600°K , 62 kcal/mole, 24 eu/mole, respectively. Later work by Harrison²⁵ gave normal boiling points and heat of vaporization for several rare earth chlorides and bromides which were from 3 to 9 kcal/mole higher in heats of vaporization and about 200° higher in boiling points than Brewer's estimated values. Trombe,²⁶ Jantsch and coworkers,²⁷ and Klemm and coworkers²⁸ have shown that the volatilities of the rare earth halides increase with increasing anionic radius and decreasing cationic radius. If Harrison's data are correct, the radius ratio correlations indicate that the heat of vaporization and normal boiling point of cerium fluoride should be several kcal/mole and about 300° higher than our calculated values, respectively. Harrison²⁵ indicated a large probable uncertainty in his work and the measured pressures that he found may be somewhat lower than the true values.

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