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Publication Date

1965-09-20

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AEC Contract No. W-7405-eng-48

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Mahn Jick Lim and Alan W. Searcy

September 20, 1965

VAPOR PRESSURE AND HEAT OF SUBLIMATION
OF CERIUM(III) FLUORIDE¹

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ABSTRACT

The vapor pressure of CeF_3 is found by the torsion-effusion method to be given at 1370 to 1685°K by the expression

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

where P is the pressure in atmospheres and the quoted errors are the standard deviation from the least-squares fit. Extrapolations yield a calculated normal boiling point of $2472^\circ \pm 80^\circ\text{K}$ and a heat of sublimation at 298.15°K of 99.5 ± 3 kcal/mole by the third-law method and 99.3 ± 3 kcal/mole by the second-law method. Most of the uncertainty in the third-law value arises from uncertainties in estimation of free energy functions for CeF_3 gas.

INTRODUCTION

Few thermodynamic data for rare earth compounds are available, and apparently no quantitative vapor pressure data have yet been reported for fluorides of rare earth compounds. This paper reports the results of measurements of the vapor pressure of cerium(III) fluoride by the torsion-effusion method.^{2,3}

EXPERIMENTAL

Cerium(III) fluoride, prepared by the reduction of ceric oxide by anhydrous hydrogen fluoride at 850°C, was supplied by Semi-Elements, Inc. The apparatus and methods employed in the research were essentially similar to those described by Searcy and Freeman.⁴ But heat was supplied to the graphite torsion effusion cells in the present study by radiation from two tantalum half cylinders which were heated by passage of an alternating electric current which formed a cylindrical hot zone of 7.6 cm diam. Tantalum radiation shields, pierced with holes to permit admission of the cell support wire at the top and to permit viewing of the cell from the bottom, closed the top and bottom of this cylinder.

A tungsten ribbon, 0.0127 cm wide, 0.00254 cm thick, and 45 cm long, was used as the torsion fiber. 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. Corrections for the effect of the finite channel

length on the force⁵ were obtained from the note of Schulz and Searcy.⁶

Temperatures of the cell were measured with an optical pyrometer. A black-body hole that had been drilled in the bottom of the cell block could not be seen through the pyrometer 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. The pyrometer used was newly calibrated by the Standards Laboratory of the Lawrence Radiation Laboratory.

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. After about 1300°K was reached, a much faster power increase was possible with the pressure still held below 5×10^{-5} torr than could be maintained at lower temperatures. The gas evolved below 1300°K may have been largely water of hydration. Staritzky and Asprey⁷ and Batsanova et al.⁸ have demonstrated that heating hydrated rare earth fluorides for an hour at 1273° to 1300°K yields the anhydrous salts.

The torsion-effusion cell was allowed to remain at 1650°K for about an hour before deflection and temperature data were taken. However, if samples already used in a previous run and kept in the system under vacuum were reheated, only about 20 min were required to heat to 1650°K and only about 15 min were needed at this temperature before measurements were begun.

After heating to 1300°K or higher, the original fine granular sample was sintered and orange-brown in color. Heating for longer periods of time at 1600°K made the sample optically anisotropic. Staritzky et al.⁷ and Batsanova et al.⁸ have previously observed the development of optical anisotropy for rare earth metal fluorides as a result of heating 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. 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.

To establish that the pressures measured in the effusion experiments were not produced by vaporization of salts of metals present as impurities, a sample was placed in a graphite crucible and heated in an induction furnace at about 1650°K at pressures below 5×10^{-5} torr until about two-thirds of the 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. The sublimate, the residual material in the cell, and a sample of the untreated cerium(III) fluoride were spectrographically analyzed by the American Spectrographic Laboratories. The major impurities reported for the sublimate were 1 to 2% each of magnesium, lanthanum, and neodymium and 6% silicon. The silicon was presumably a contaminant from the collection disk since the silicon content of the original sample was below the limit of detection. The 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. Measured pressures are shown in Table II and Fig. 1.

A more detailed description of the apparatus and techniques is given elsewhere.⁹

RESULTS AND DISCUSSION

Studies¹⁰⁻¹² 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 , is below 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 II 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 approximation¹³ with the molecular diameter of cerium(III) fluoride taken as 7.36Å, a value calculated from the ionic radii with the molecule assumed 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 because systematic deviations in heats appeared to occur at smaller values of λ/d .

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 pressure of cerium(III) fluoride in atmospheres for those data with λ/d ratios larger than 0.2:

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

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 $\text{CeF}_3(\text{s})$ King and Christensen¹⁴ report heat capacity, enthalpy and entropy data, and Westrum and Beale¹⁵ report $\Delta S_{298} = 27.54$ cal/deg/mole, in good agreement with 27.6 ± 0.2 cal/deg/mole reported by King and Christensen.

The only significant vapor species is believed to be $\text{CeF}_3(\text{g})$. Brewer¹⁶ showed that dimer vapor species are found for trihalides only 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 unlikely. Thermodynamic calculations

indicate that the partial pressures of $\text{CeF}(g)$, $\text{CeF}_2(g)$, $\text{CeF}_4(g)$, $\text{Ce}(g)$ and $\text{F}_2(g)$ which may be produced by various disproportionation and decomposition reactions are probably several orders of magnitude smaller than the observed pressures; also, the pressures of $\text{CF}_4(g)$, $\text{C}_2\text{F}_6(g)$ and $\text{C}_2\text{F}_4(g)$ which may be produced by the reaction of the sample with the graphite cell are probably all several orders of magnitude below the observed pressures.

In order to calculate heat capacities and free energy functions for $\text{CeF}_3(g)$, molecular constants were estimated. Batsanova et al.⁸ observed a strong absorption spectrum at 410 cm^{-1} in crystalline CeF_3 and attributed the band to valence vibration of the Ce-F bond. In AlF_3 crystal, the observed Al-F valence vibrational frequency is 615 cm^{-1} , while for AlF_3 gas molecule the calculated stretching vibrational frequency is reported to be 640 cm^{-1} .¹⁷ The molecular shape of $\text{CeF}_3(g)$ is assumed to be the same as $\text{AlF}_3(g)$, i.e., a planar triangle, point group D_{3h} . The estimation of the symmetrical stretching vibrational frequency¹⁸ of $\text{CeF}_3(g)$ is made from the valence vibrational frequency of $\text{CeF}_3(s)$ by multiplying by 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 $2.04 \times 10^{-5} \text{ dyn/cm}$.

As a check, an empirical relationship reported by Herschbach and Laurie¹⁹ was used to calculate $1.83 \times 10^5 \text{ dyn/cm}$. In order to apply the Herschbach and Laurie relationship, values of their empirical constants a_{ij} and b_{ij} and of the Ce-F bond distance were required. The value of a_{ij} was estimated to be 2.24 and of b_{ij} to be 0.57, and the

bond distance was estimated by means of an empirical relationship of Pauling²⁰ between distances in solids and gases to be $2.09\text{\AA}$.

A semilogarithmic plot of the two bending force constants vs stretching force constants for several known molecules^{17,18} 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 $k_\delta/l^2 = 0.105 \times 10^5$, where k_Δ is the out of plane bending force constant, k_δ is the in-plane bending force constant, and l is the equilibrium distance between cerium and fluorine atoms, were obtained. Valence-force model calculation¹⁸ 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. Brewer et al.²¹ showed that this approximation yielded good results for thermodynamic calculations when applied to dihalides of transition metals. The ground state of Ce^{+3} is $^2F_{5/2}$.²² The first excited level is $^2F_{7/2}$ at 2253 cm^{-1} .²² Contributions from higher levels are insignificant for the temperature range of this work.

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 $\text{CeF}_3(\text{g})$. Calculated heat capacities and free energy functions are given in Table III. A least-squares calculation by the second law method yields $-R \ln P = (97.78 \pm 0.59) \times 10^3/T - 35.47 \pm 0.39 - 2.31 \ln T + 4.83 \times 10^{-3} T + 1.86 \times 10^5 T^{-2}$ where quoted

errors are the standard deviations. From this expression, the second-law value of $\Delta H_{298}^{\circ} = 99.29 \pm 0.59$ kcal/mole was obtained. If the temperature scale is assumed to be in error by $+5^{\circ}$ at the upper end of our temperature range and in error by -5° at the lower end, the value of ΔH_{298}° calculated by the second law method is changed by 2 kcal. The total uncertainty in the second law value is estimated to be ± 3 kcal.

The average third-law value calculated for ΔH_{298}° and the standard deviation for 84 measurements between 1370 and 1631°K are 99.51 ± 0.25 kcal/mole. For the 14 measurements for which λ/d values were calculated to be smaller than 0.2, ΔH_{298}° was calculated to be 99.03 ± 0.79 kcal/mole. The lower average heat for these measurements probably reflects deviation 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 values of the heat of sublimation at 298°K calculated by the third law method.

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, heat of fusion, and liquid heat capacity of cerium(III) fluoride were reported to be 1710°K ,²³ 13.20 kcal/mole,¹⁴ and 32.00 cal/deg/mole,¹⁴ respectively. Combining these values with the second-law equation of this work, the vapor pressure in the liquid range may be expressed as $-R \ln P = (93.93 \pm 0.59) \times 10^3/T - 129.55 \pm 1.07 + 11.79 \ln T - 0.24 \times 10^{-3} + 1.32 \times 10^5 T^{-2}$ where quoted errors are the standard deviations. From this expression, the normal boiling point of $2472 \pm 80^\circ\text{K}$ and the heat and entropy of vaporization, 66.4 kcal/mole and 26.9 eu/mole, at the normal boiling point were obtained.

ACKNOWLEDGMENT

This work was supported by the U. S. Atomic Energy Commission.

REFERENCES

1. From the thesis submitted by Mahn Jick Lim in partial fulfillment of the requirements for the M.S. degree in Engineering Science at the University of California, June, 1965.
2. H. Mayer, Z. Physik, 67, 240 (1931).
3. M. Vollmer, Z. Physik. Chem., Bodenstein Festband, 863 (1931).
4. A. W. Searcy and R. D. Freeman, J. Am. Chem. Soc., 76, 5229 (1954).
5. R. D. Freeman and A. W. Searcy, J. Chem. Phys., 22, 762 (1954).
6. D. A. Schulz and A. W. Searcy, J. Chem. Phys., 36, 3099 (1962).
7. E. Staritzky and L. Asprey, Anal. Chem., 29, 855 (1957).
8. L. P. Batsanova, G. N. Grigor'eva, and S. S. Batsanov, Zh. Strukt. Khim., 4 [1], 37 (1963).
9. D. A. Schulz and A. W. Searcy, J. Phys. Chem., 67, 103 (1963).
10. H. W. Liepmann, J. Fluid Mech., 10, 65 (1961).
11. A. W. Searcy and D. A. Schulz, J. Chem. Phys., 38, 772 (1963).
12. K. D. Carlson, P. W. Gilles and R. J. Thorn, J. Chem. Phys., 38, 2064 (1963).
13. S. Dushman, Scientific Foundations of Vacuum Technique (John Wiley and Sons, Inc., New York, 1949), Ch. 1.
14. E. G. King and A. L. Christensen, U. S. Bur. Mines Bull. 5510 (1959).
15. E. F. Westrum, Jr., and A. F. Beale, Jr., J. Phys. Chem., 65, 353 (1961).
16. L. Brewer, The Fusion and Vaporization Data of the Halides, Paper 7, in Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, L. L. Quill, Ed., National Nuclear Energy Series, IV-19B (McGraw-Hill

- Book Co., New York, 1950), pp. 193-275.
17. JANAF Thermochemical Data, Dow Chemical Company, Midland, Michigan, 1963.
 18. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1959).
 19. D. R. Herschbach and V. W. Laurie, J. Chem. Phys., 35, 458 (1961).
 20. L. Pauling, The Nature of the Chemical Bond, 3rd Ed. (Cornell University Press, Ithaca, 1960).
 21. L. Brewer, G. R. Somayajulu, and Elizabeth Brackett, Chem. Rev., 63, 111 (1963).
 22. M. A. El'Yashevich, Spectra of the Rare Earths, Book 2, 1953 (AEC-tr-4403, 1961).
 23. B. Porter and E. A. Brown, J. Am. Ceram. Soc., 45, 49 (1962).

Table I. Orifice dimensions.*

Cell	Hole diameter (cm)		Lid thickness (cm)	
	(1)	(2)	(1)	(2)
1	0.0779	0.0813	0.0993	0.1039
2	0.1384	0.1241	0.1052	0.1021
3	0.2518	0.2528	0.1026	0.1024

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

Table II. 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	1.228×10^{-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 II. (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	59.50
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 II. (cont.)

Temp (°K)	Pressure (atm)	λ/d	ΔH_{298}° (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.

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

Temp (°K)	C _p (cal/deg/mole)	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$ (cal/deg/mole)
298.15	17.630	77.966
500	19.132	80.023
1000	20.612	87.561
1300	20.830	91.377
1400	20.841	92.647
1500	20.835	93.643
1600	20.808	94.670
1710	20.784	95.778
1800	20.746	96.599

Figure Caption

Figure 1. Vapor Pressure of Cerium(III) Fluoride

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