Title

THE VAPOR PRESSURE HEAT OF SUBLIMATION, AND EVAPORATION COEFFICIENT OF LANTHANUM FLUORIDE

Permalink

https://escholarship.org/uc/item/7x72c683

Authors

Mar, Raymond W.
Searcy, Alan W.

Publication Date

1966-08-01

University of California

Ernest O. Lawrence Radiation Laboratory

THE VAPOR PRESSURE, HEAT OF SUBLIMATION, AND EVAPORATION COEFFICIENT OF LANTHANUM FLUORIDE

J. Phys. Chem.

UCRL-16649-Rev.

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7408-eng-48

THE VAPOR PRESSURE, HEAT OF SUBLIMATION, AND EVAPORATION COEFFICIENT OF LANTHANUM FLUORIDE

Raymond W. Mar and Alan W. Searcy

August, 1966

THE VAPOR PRESSURE, HEAT OF SUBLIMATION, AND EVAPORATION COEFFICIENT OF LANTHANUM FLUORIDE

Raymond W. Mar and Alan W. Searcy

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Mineral Technology, College of Engineering,
University of California, Berkeley, California

August 3, 1966

ABSTRACT

The vapor pressure of solid lanthanum fluoride in the temperature range 1325° to 1650°K has been found by the torsion-effusion method to be given by the equation $\log_{10} P_{atm} = -(2.173 \pm 0.009) \times \frac{10^4}{T} + 9.608 \pm 0.065$. Estimated heat capacities and free energy functions were used with the measured pressures to calculate the heat of sublimation at 298.15°K by the Second and Third Law methods. The values are 107 ± 5 kcal and 103 ± 5 kcal respectively. Because of uncertainties in estimates, 107 ± 5 kcal is set as the most probable value and uncertainty. Comparison of torsion-Langmuir measurements from the (0001) crystal faces with the effusion data yield an evaporation coefficient of 0.95 ± 0.1 in the experimental range.

I. INTRODUCTION

Accurate thermodynamic data for most of the rare earth fluorides are still not available, although Brewer[1] has estimated data for most of them. Lim and Searcy[2] have studied the vaporization of cerium trifluoride by the torsion-effusion method. Mass spectrometric studies have been made on the trifluorides of scandium, yttrium, and lanthanum by Kent, Zmbov, Kana'an, Besenbruch, McDonald, and Margrave[3].

This paper reports a torsion-Langmuir and torsion-effusion[4,5] investigation of lanthanum fluoride in the temperature range from 1325° to 1650°K. From the effusion measurements the heat of sublimation at 298.15°K has been calculated by the Second and Third Law methods and from comparison of Langmuir and effusion measurements the evaporation coefficient has been determined in the experimental temperature range. Apparently, no previous study of the evaporation coefficient of a halide of a main group III element has been reported.

II. EXPERIMENTAL

A graphite cell with two eccentrically placed orifices was suspended in a furnace by a 0.005 cm diameter tungsten fiber of about 43 cm length. The torsion cell used for the Knudsen studies consisted of a cell block, two cylindrical cells, and two cell end plates, all of graphite. The cells fit snuggly into holes in the side faces of the cell block. The cell end plates had orifices drilled through the centers through which vapor could escape. The torsion cell used for the Langmuir studies was modified to allow the LaF_3 crystal surfaces to be held flush against inner faces of orifice lids by graphite back-up washers. All gaseous molecules escaping from crystal surface areas other than those exposed by the orifices were vented out through a 35 mm hole in the top of the torsion cell block. Pressures can be calculated by means previously described from angular deflections caused by vaporization in effusion[6,7] and Langmuir experiments[8]. Observed pressures must be corrected for the effect of orifice dimensions[9,10].

For the present study, the Knudsen orifices were cylindrical and the Langmuir orifices were conically concaved with an apex angle of 120°. The dimensions and correction factors for the various orifices are given in Table I. To minimize the possibility of a systematic error, the suspending fiber was replaced three times. The torsion constants of the wires were 2.144, 2.062, 1.979, and 1.982 dyne-cm/rad.

The cells were heated in a resistance furnace by radiation from tungsten hairpin-shaped elements. A non-magnetic stainless steel column enclosed the suspension system.

As escape of vapor caused the cell to rotate in one direction, it was manually returned to its original position by twisting the upper point of attachment of the fiber in the opposite direction. The angles of twist necessary to return the cell to its original orientation were recorded to the nearest five-thousandths of a degree by means of a modified ganiometer.

Temperatures were read by means of an optical pyrometer which was focused on a black body hole drilled into the bottom of the cell block. Temperature gradients in the Knudsen and Langmuir cells are believed to have been negligible because (1) cells were suspended in the central portion of an 8 cm vertical zone for which the temperature had been demonstrated to be constant to within 2°C and (2) optical pyrometer measurements revealed no variation in temperature across the bottom surface of the cell.

About a 10° discrepancy was noticed between the temperatures read on the low-scale and the high-scale of the calibrated pyrometer. The pyrometer was accordingly recalibrated by comparison with platinum-platinum/10% rhodium thermocouple measurements. For these recalibrations a graphite cell was heated in the furnace with the thermocouple placed in the cell within 0.6 cm of the black body hole.

The low-scale pyrometer readings agreed exactly with the thermocouple at 1025°C but deviated by 10° at 1225°C. The high-scale agreed exactly at 1200°C but deviated by 7° at 1375°C. Correction of pyrometer readings to agree with the temperatures read with the thermocouple improved agreement between data obtained with the two different pyrometer scales.

It should be noted that the errors in the uncorrected pyrometer readings did not exceed the error limits claimed by the manufacturer, yet because the errors were temperature dependent they could cause a relatively large error in the determination of a heat of sublimation from measurements of the temperature dependence of the vapor pressure. A Second Law heat of sublimation calculated from uncorrected measurements made only with the low-scale would be in error by 3%.

The validity of the calibrations was checked by measuring the vapor pressure of tin. Thirty-three tin datum points yielded an average Third Law heat of sublimation of 71.98 kcal/mole, which is in good agreement with the values of 71.8 and 72.2 reported by Schulz[11] and Hultgren[12].

Prior to each series of effusion measurements with lanthanum fluoride, the cell was tested for leaks of a kind that might contribute to the measured angle of deflection. Lanthanum fluoride was loaded into a pair of cells which had no orifices. The assembly was then heated to 1600°K and absence of significant leakage was demonstrated by absence of rotational deflections. Upon completion of the test, orifices were drilled into the cell end plates.

Each new sample was heated slowly to 1650°K and held at that temperature for one hour to vaporize volatile impurities. Data were then collected by making either random temperature changes of about 40° or by making smaller successive temperature increases or decreases. The background pressure for all measurements was between 1×10^{-9} and 7×10^{-9} atm.

The lanthanum fluoride powder of 99.9% purity used in the Knudsen experiments was purchased from Semi-Elements Inc. To ensure that the pressure data were due to the vaporization of lanthanum fluoride only, samples of the original material, of a characteristic sublimate from heating at 1600°K and of residue were analyzed spectrographically. The analyses performed by the American Spectrographic Laboratories showed lanthanum to be the principal metallic constituent in both starting material and sublimate. The principal impurity in the starting material was 0.015% iron where the impurity is reported as the oxide of iron. The sublimate contained 0.3% silicon (presumably from the quartz walls on which the sublimate was collected) and 0.03% iron as the principal metallic impurities. The physical appearance of the sample changed markedly upon heating, despite the fact that spectroscopic and x-ray analyses showed no measurable changes. The originally flaky white powder was consolidated into a dense grey mass. Heating to temperatures above 1500°K for times of two hours or more resulted in production of crystallites up to 0.3 mm on a side.

The lanthanum fluoride crystal used in the Langmuir experiments was purchased from Nuclear Elements Corporation. The crystal of unknown orientation was oriented by the back-reflection Laue method. Despite a report of easy basal cleavage by Weller and Kucza,[13] trial and error attempts to find a plane of cleavage failed. Crystal slices about 1.5 mm thick were made along the basal plane by means of a diamond saw with kerosene coolant. Each crystal slice was polished with four successive grades of emery paper. A final polish was accomplished with 100 micron alumina grit in a kerosene medium.

III. RESULTS AND DISCUSSION

The results of 100 Knudsen vapor pressure determinations collected in the range 1325° to 1650°K are presented in Table II and Fig. 1. The results of 21 free surface pressure determinations are given in Table III and Fig. 1. A least squares fit of the effusion data yielded the equation:

$$\log_{10} P_{atm} = -(2.173 \pm 0.009) \times \frac{10^4}{T} + 9.608 \pm 0.065 \qquad (1)$$

where the errors are standard deviations.

The vapor was assumed to consist only of LaF_3 molecules. This is the molecule indicated to be the principal vapor species by the mass spectrometric study of Kent, et al.[3] Furthermore, thermodynamic calculations indicate that partial pressures of other species, LaF, LaF_2, CF_4,

C_2F_4, C_2F_6, La, and F_2, which might be produced by dissociation or reaction with carbon, should be negligible. The possibility that the vapor was $H_2O(g)$ or lanthanum-oxygen products from a partially hydrated sample was eliminated by the one hour heat treatment at 1650°K. It has been shown that hydrated rare earth fluorides are completely dehydrated by such treatment.[14, 15]

Because it has been shown that too low a λ/d ratio implies the inapplicability of molecular flow equations,[16,17] the ratio of the mean free path to the orifice diameter, λ/d, was calculated at all readings by means of a hard sphere approximation[18] with the sphere radius taken as the sum of the experimental La-F distance[19] and the fluoride ion radius. In this research, in which the lowest value of λ/d was 0.40, no indications of a significant change in flow characteristics with λ/d was observed..

The heat of sublimation was calculated from the effusion data by the Second Law and Third Law methods.[20] The Third Law method requires knowledge of free energy functions and the Second Law method requires heat capacity data. It was necessary to estimate these quantities for both the solid and the gas.

The heat capacity of crystalline lanthanum fluoride was estimated to be $C_p = 19.77 + 8.48 \times 10^{-3}T - 5.90 \times 10^{4}T^{-2}$ eu/mole by assuming that the difference between the heat capacities of La_2O_3[21] and $2(LaF_3)$ is the same as the difference between the heat capacities of Ce_2O_3[22] and $2(CeF_3)$.[23]

The La-F valence vibration in crystalline LaF_3 is reported to be 403 cm^{-1}[15]. The La-F stretch frequency for gaseous LaF_3 was estimated to be 419 cm^{-1} on the assumption that the ratio of the valence vibration frequency in the crystalline state to the stretch frequency in the gaseous state is the same as the ratio for AlF_3.[24] The stretching force constant for La-F bonds in the gaseous molecules is then calculated to be 1.96 x 10^5 dyne/cm. Lim and Searcy[2] have shown that for CeF_3 this means for estimating the fore constant gives a result that differs by only 10% from that calculated from an independent empirical equation formulated by Herschbach and Laurie.[25]

Plots of the out-of-plane bend force constant $\ell n(k_2/l^2)$ and the in-plane bend force constant $\ell n(k_3/\underline{l}^2)$, where $\underline{l}$ is the La-F distance, versus k_1 for the constants of D_{3h} point group species, show a straight line relationship. $k_2/\underline{l}^2$ and $k_3/\underline{l}^2$ for LaF_3 were assumed to fall on this line. These force constants were thus estimated to be 0.192 x 10^5 and 0.103 x 10^5 dyne/cm. Using the three force constants and the valence-force model,[26] the vibrational frequencies for $LaF_3(g)$ were calculated to be 419, 156, 461(2) and 179(2) cm^{-1}.

The electronic contribution to the heat capacity was assumed to be the same as that of La^{+3} ion.[27] Brewer et al[28] have shown that for transition metal dihalides, values so estimated are in reasonable agreement with known data. Heat capacities for the gas were calculated at 100° intervals from 300° to 1800°K and the equation, $C_p = 21.42 - 4.06 \times 10^{-4}T - 3.38 \times 10^5 T^{-2}$ eu/mole was fitted to the values.

The free energy functions for the crystalline state were calculated from the estimated heat capacity and Glassner's[29] estimate of S°_{298} = 27.0 eu/mole. Glassner's entropy estimate for CeF_3 was only 0.04 eu smaller than the experimental value found by Westrum and Beale.[30] The probable error in the estimate of S°_{298} for LaF_3(s), 0.2 eu, could cause a 0.3 kcal/mole error in the calculated heat of sublimation. The estimated free energy functions for lanthanum fluoride between 1000° and 1800° are given in Table IV. The average Third Law value for the heat of sublimation over all datum points was 103.48 ± 0.35, where the error is the standard deviation from the mean.

A least squares calculation gave $\Delta H^\circ_1/T + I = (106.424 \pm 0.440) \times 10^3/T - 43.291 \pm 0.302$ from the Second Law data from which $\Delta H^\circ_{298.15} = 107.45 \pm 0.44$ kcal/mole and $\Delta S^\circ_{298.15} = 53.24 \pm 0.30$ eu were obtained.

The major sources of error in calculated heats of sublimation were the estimations of the heat capacities and free energy functions. Estimated errors of 10% of the vibrational frequencies, 5% of the molecular radius, and 15% of the electrical contribution to the free energy function cause an error of 1% of the gaseous free energy function. Assuming the solid heat capacity and S°_{298} to be in error by 1 cal/mole and 0.2 eu/mole leads to an error of 2.0% of the solid free energy function. Errors in calibrating the wire, measuring the orifice diameter, channel length, and axis arms, and reading the angles of deflection could cause an error of about 0.5% of the ΔH°_{298}. The temperatures are believed to be correct to within ±5°. An error of ±5° causes an error of ±0.5% in the heat of sublimation. As a result, the Third Law heat of sublimation is estimated to be correct within ±4 kcal/mole.

The estimated errors in the molecular constants cause a 0.2 cal/mole error in the gaseous heat capacity. An assumed error of 1 cal/mole in the heat capacity for the solid causes an uncertainty of ±0.5 kcal/mole in the Second Law heat of sublimation. The assumption that the temperature scale was in error by -5° at the lower end of the experimental range and by +5° at the high end causes an error of -3 kcal in ΔH°_{298}. The Second Law heat of sublimation is therefore estimated to be accurate to within ±4 kcal/mole.

The discrepancy between the Third Law and Second Law heats of sublimation probably results mainly from inaccuracies in the estimated free energy functions and in the temperature dependence of the pressure measurements. Until more experimental data for molecular constants of high temperature gas molecules become available, the Second Law results should probably be considered more reliable, and the heat of sublimation at 298.15°K can be conservatively fixed as 107 ± 5 kcal/mole.

The sublimation pressures for lanthanum fluoride measured recently by Kent, et al[3] lie about a factor of two below pressures reported in this paper. Kent, et al used Langmuir weight loss measurements and mass spectrometric measurements calibrated by use of the Langmuir weight loss data. Discrepancies of about a factor of two have also been noted between data for CaF_2 and BaF_2 collected in Margraves laboratory[31,32] and data of Schulz[16] and Hart[33] respectively. There appears to be a systematic discrepancy between data collected by the torsion-effusion method in this laboratory and data collected by or normalized with Langmuir measurements in Margrave's laboratory. A systematic error of a factor of two in pressure determinations would contribute about 2 kcal error to a Third Law heat of sublimation for lanthanum fluoride and negligible error to a Second Law heat of sublimation.

The uncertainty in the determination of the evaporation coefficient was greatly reduced by collecting the equilibrium pressure data and the free surface sublimation data in the same apparatus by the same techniques so that most systematic errors in pressure determinations would be common to both sets of data and would cancel in calculations of the coefficient. It is seen on Fig. 1 that the torsion-Langmuir data are in very close agreement with the effusion data. Comparison of the Langmuir pressures with the equilibrium pressures given by Eq. (1) shows no significant temperature dependence of the evaporation coefficient and yields a coefficient of 0.95 ± 0.12, the error being the standard deviation from the mean. The estimated experimental error in the determination of the evaporation coefficient is ±0.1 and is attributed primarily to a ±5° uncertainty in the surface temperature of the lanthanum fluoride crystal relative to the temperature in an effusion cell.

A microscopic examination of the evaporated Langmuir surfaces showed them to be essentially planar but irregular. The 1 mm surfaces were flat with no surface irregularities. The 1.5 mm surfaces consisted of about 40% flat areas and 60% made up of many mountain shaped features that averaged 1.5 x 10^4 sq. microns in basal area and 50 microns in height. The 3 mm surfaces were planar with a fine network of surface irregularities estimated to be about 10 microns in height.

The samples were reheated to 1200°C for 15 minutes and re-examination showed that all surfaces tended to smooth out. The rather large peaks on the 1.5 mm surface decreased in height and the amount of flat area increased twofold. The 3 mm surfaces exhibited an increase in the amount of flat area and the surface irregularities were reduced to a fine, almost linear network of raised area. For evaporation from the (0001) plane of lanthanum fluoride, the difference between the apparent evaporation coefficient (that measured without correction for surface irregularities) and the true evaporation coefficient is probably less than 1%. To determine if the apparent pressures from a given area of surface changed measurably as the surface receded during evaporation, data were collected with the 1 mm orifice until a recess 1 mm deep formed. The sides of the cavity were vertical. No change in the pressure-temperature relationship was observed as the cavity deepened. This fact further substantiates the conclusion that the evaporation coefficient is near unity. If the coefficient were much less than unity, the Langmuir pressures would have increased noticeably with time because the deepening cavity would provide an increasingly close approximation to an effusion cell.

We conclude that the evaporation coefficient for the (0001) plane of lanthanum fluoride is unity to within a small probable error and that evaporation coefficients for other tri-fluorides of lanthanum and main group three elements are probably close to unity as well.

Burns[34] has recently reported convincing evidence that the evaporation coefficients for the various vapor species from solid Al_2O_3, solid Ga_2O_3, and solid Im_2O_3 approach 1/3 as a limiting value at the melting point. He points out that Hirth and Pound[35] have predicted that surface diffusion would set an upper limit of $\alpha = 1/3$ for single crystals of metals, and he draws attention to the fact that several other studies in addition to his own support the hypothesis that a similar limit may apply to many inorganic solids. The present research and the recent study of barium fluoride sublimation demonstrate that no such limit applies for some inorganic solids. Further study is needed to ascertain why for some inorganic solids the evaporation coefficient may be unity over a considerable temperature range and for others it does not reach unity in a realizable temperature range.

REFERENCES

1. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials--Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Co., Inc., New York (1950).
2. M. J. Lim and A. W. Searcy, J. Phys. Chem., 70, 1762 (1966).
3. R. A. Kent, K. F. Zmbov, A. S. Kana'an, G. Besenbruch, J. D. McDonald, and J. L. Margrave, unpublished work (1965).
4. H. Mayer, Z. Physik 67, 240 (1931).
5. M. Vollmer, Z. Physik. Chem., Bodenstein Festband, 863 (1931).
6. A. W. Searcy and R. D. Freeman, J. Am. Chem. Soc. 76, 5229 (1954).
7. D. J. Meschi and A. W. Searcy, J. Phys. Chem., 63, 1175 (1959).
8. Z. A. Munir and A. W. Searcy, J. Electro. Chem. Soc., 111, 1170 (1964).
9. R. D. Freeman and A. W. Searcy, J. Chem. Phys. 22, 762 (1954).
10. R. D. Freeman, "Molecular Flow and the Effusion Process in the Measurement of Vapor Pressures," ASD-TDR-'63-754 (1963).
11. D. A. Schulz, Ph.D. Thesis, University of California, Berkeley, 1961.
12. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, Selected Values of Thermochemical Properties of Metals and Alloys (John Wiley and Sons, Inc., New York, 1963).
13. P. F. Weller and J. A. Kucza, J. App. Phys. 35, 1945 (1964).
14. E. Staritsky and L. Asprey, Anal. Chem. 29, 855 (1957).
15. L. P. Batsanova, G. N. Grigor'eva, and S. S. Batsanov, Zh. Strukt. Khim. 4, 37 (1963).
16. D. A. Schulz, and A. W. Searcy, J. Chem. Phys. 38, 772 (1963).

17. K. O. Carlson, P. W. Gilles, and R. J. Thorn, J. Chem. Phys., 38, 2064 (1963).

18. S. Dushman, Scientific Foundations of Vacuum Technique (John Wiley and Sons, Inc., New York, 1949).

19. P. A. Akishin and V. A. Naumov, Khim. i Khim. Tekhnol. (1959).

20. G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, "Thermodynamics", McGraw-Hill Book Co., Inc., New York (1961).

21. J. O. Blomoeke and W. T. Ziegler, J. Am. Chem. Soc. 73, 5099, (1951).

22. F. A. Kuznetsov and T. N. Rezukhina, Zh. Fiz. Khim. 35, 956, (1961).

23. E. G. King and A. L. Christensen, U. S. Bur. Mines Bull. RI 5510 (1959).

24. JANAF Thermochemical Data, Dow Chemical Company, Midland, Michigan (1963).

25. D. R. Herschbach and V. Z. Laurie, J. Chem. Phys. 35, 458 (1961).

26. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1959).

27. M. A. El'Yashevich, Spectra of the Rare Earths, Book 2, 1953 (AEC-tr-4403, 1961).

28. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev. 63, 111 (1963).

29. A. Glassner, The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750.

30. E. F. Westrum, Jr., and A. F. Beale, Jr., J. Phys. Chem. 65, 353 (1961).

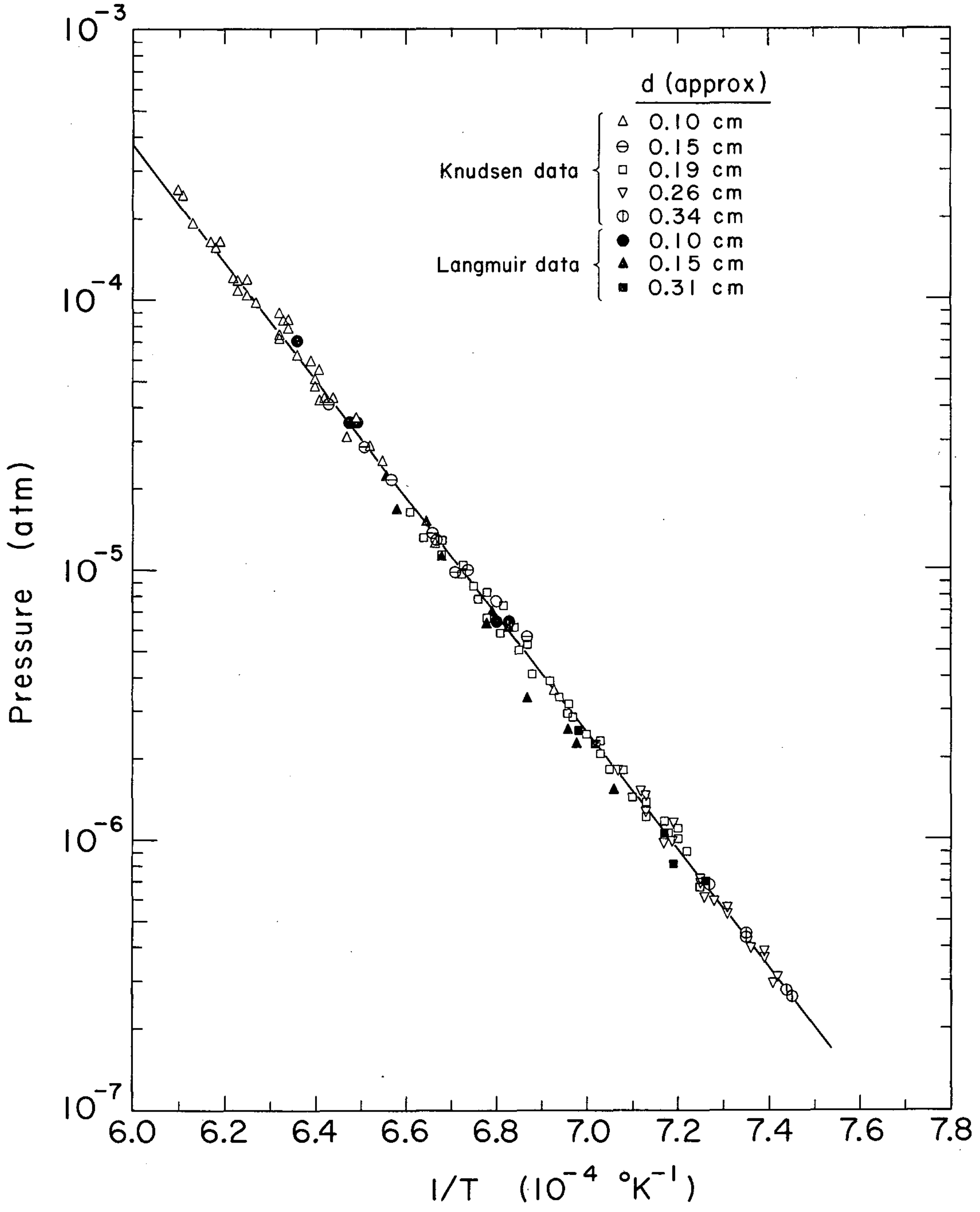
31. G. D. Blue, T. C. Ehlert, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).

32. G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, J. Phys. Chem. 67, 877 (1963).

33. P. E. Hart and A. W. Searcy, J. Phys. Chem. in press.

34. Richard P. Burns, J. Chem. Phys. 44, 3307 (1966).

35. J. P. Hirth and G. M. Pound, J. Chem. Phys. 26, 1216 (1957).



d (approx)
Knudsen data
△ 0.10 cm
⊖ 0.15 cm
□ 0.19 cm
▽ 0.26 cm
⦶ 0.34 cm
Langmuir data
● 0.10 cm
▲ 0.15 cm
■ 0.31 cm
Pressure (atm)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
1/T (10^{-4} °K^{-1})

MUB-9680

Figure Caption

Figure 1. Vapor pressure of lanthanum fluoride.

Table I. Orifice dimensions

Cell	Orifice diameter (cm)		Apex Angle	Channel length (cm)		Correction factors	
	(a)	(b)		(a)	(b)	(a)	(b)
Knudsen 1	0.0990	0.0986	-	0.1499	0.1524	0.4697	0.4645
Knudsen 2	0.1594	0.1524	-	0.1633	0.1591	0.5508	0.5621
Knudsen 3	0.1866	0.1940	-	0.1628	0.1631	0.6063	0.6155
Knudsen 4	0.2633	0.2634	-	0.1506	0.1491	0.7043	0.7067
Knudsen 5	0.3452	0.3529	-	0.1613	0.1621	0.7465	0.7500
Langmuir 1	0.0999	0.0982	120°	0.3144	0.3172	1.129	1.130
Langmuir 2	0.1525	0.1517	120°	0.3172	0.3172	1.122	1.122
Langmuir 3	0.3056	0.3213	120°	0.3172	0.3172	1.104	1.102

Table II. Temperature effusion pressure, ratio of mean free path to orifice diameter, and the Third Law heat of sublimation of LaF_3.

Temp (°K)	Pressure (atm)	Mean free path/Diameter	$\Delta H^\circ_{298.15}$ (kcal/mole)
<u>0.10 cm diameter orifice</u>			
1540	3.683×10^{-5}	2.58	102.81
1559	5.484×10^{-5}	1.76	102.86
1582	8.915×10^{-5}	1.10	102.59
1577	7.819×10^{-5}	1.25	102.70
1579	8.256×10^{-5}	1.18	102.65
1578	8.318×10^{-5}	1.17	102.60
1599	1.175×10^{-4}	0.84	102.70
1615	1.623×10^{-4}	0.62	102.60
1640	2.519×10^{-4}	0.40	102.61
1638	2.407×10^{-4}	0.42	102.65
1595	9.530×10^{-5}	1.04	103.15
1622	1.616×10^{-4}	0.62	103.03
1601	1.034×10^{-4}	0.96	103.25
1609	1.184×10^{-4}	0.84	103.27
1619	1.536×10^{-4}	0.65	103.02
1582	7.375×10^{-5}	1.33	103.19
1562	4.769×10^{-5}	2.02	103.34
1572	6.175×10^{-5}	1.58	103.14
1560	4.199×10^{-5}	2.30	103.63
1540	3.050×10^{-5}	3.14	103.68
1444	3.533×10^{-6}	25.31	103.12
1472	7.382×10^{-6}	12.35	103.33
1500	1.257×10^{-5}	7.39	103.56
1521	2.007×10^{-5}	4.70	103.47
1535	2.875×10^{-5}	3.30	103.26
1566	5.895×10^{-5}	1.64	102.92
1605	1.162×10^{-4}	0.86	103.09
1528	2.501×10^{-5}	3.78	103.25
1552	4.306×10^{-5}	2.38	103.07
1557	4.315×10^{-5}	2.23	103.35
1562	5.054×10^{-5}	1.91	103.17
1582	7.158×10^{-5}	1.37	103.23
1604	1.064×10^{-6}	0.93	103.31
1631	1.925×10^{-6}	0.52	102.97

Table II. (cont.)

Temp (°K)	Pressure (atm)	Mean free path/Diameter	$\Delta H^{\circ}_{298.15}$ (kcal/mole)
0.15 cm diameter orifice			
1523	2.177×10^{-5}	2.83	103.35
1536	2.858×10^{-5}	2.18	103.34
1556	4.158×10^{-5}	1.52	103.41
1471	7.625×10^{-6}	7.82	103.19
1499	1.288×10^{-5}	4.72	103.43
1522	2.168×10^{-5}	2.84	103.31
1523	2.168×10^{-5}	2.85	103.37
1502	1.374×10^{-5}	4.43	103.43
1490	9.814×10^{-6}	6.15	103.67
1484	9.986×10^{-6}	6.02	103.23
1456	5.660×10^{-6}	10.43	103.06
0.19 cm diameter orifice			
1389	1.108×10^{-6}	40.32	103.17
1386	8.978×10^{-7}	49.65	103.58
1380	6.737×10^{-7}	65.87	103.91
1403	1.214×10^{-6}	37.14	103.89
1413	1.810×10^{-6}	25.09	103.46
1437	2.916×10^{-6}	15.84	103.72
1466	7.725×10^{-6}	6.48	103.00
1487	1.046×10^{-5}	9.57	103.26
1435	2.840×10^{-6}	16.24	103.66
1496	1.287×10^{-5}	3.74	103.24
1497	1.287×10^{-5}	3.74	103.30
1512	1.624×10^{-5}	2.99	103.54
1408	1.433×10^{-6}	31.58	103.77
1393	1.053×10^{-6}	42.54	103.60
1418	1.815×10^{-6}	25.11	103.78
1441	3.320×10^{-6}	13.95	103.77
1445	3.848×10^{-6}	12.07	103.46
1462	6.088×10^{-6}	7.72	103.26
1481	8.639×10^{-6}	5.51	103.43
1493	1.320×10^{-5}	3.64	103.16
1506	1.320×10^{-5}	3.66	103.81
1489	9.614×10^{-6}	4.98	103.66
1474	8.190×10^{-6}	5.78	103.18

Table II. (Cont.)

Temp (°K)	Pressure (atm)	Mean free path/Diameter	ΔH°298.15 (kcal/mole)
1455	5.235×10^{-6}	8.93	103.25
1436	3.173×10^{-6}	14.94	103.42
1423	2.331×10^{-6}	20.62	103.41
1474	6.607×10^{-6}	7.17	103.80
1388	1.001×10^{-6}	44.60	103.38
1394	1.173×10^{-6}	38.22	103.37
1423	2.032×10^{-6}	22.51	103.85
1431	2.434×10^{-6}	18.89	103.85
1402	1.395×10^{-6}	32.32	103.43
1443	3.754×10^{-6}	12.78	103.41
1453	4.083×10^{-6}	11.44	103.82
1459	5.000×10^{-6}	9.38	103.63
1469	5.826×10^{-6}	8.10	103.83
1479	7.739×10^{-6}	6.14	103.66
1498	1.137×10^{-5}	4.24	103.74
1470	7.944×10^{-6}	5.95	103.03
<u>0.26 cm diameter orifice</u>			
1395	9.670×10^{-7}	33.52	103.97
1373	5.971×10^{-7}	53.44	103.76
1354	3.638×10^{-7}	86.44	103.74
1349	2.942×10^{-7}	106.62	103.97
1359	4.086×10^{-7}	77.21	103.79
1379	6.904×10^{-7}	46.44	103.78
1388	9.800×10^{-7}	32.91	103.45
1391	1.170×10^{-6}	27.63	103.16
1403	1.469×10^{-6}	22.18	103.36
1414	1.836×10^{-6}	17.88	103.49
1404	1.513×10^{-6}	21.55	103.33
1369	5.703×10^{-7}	55.77	103.53
1354	3.943×10^{-7}	79.85	103.53
1347	3.115×10^{-7}	100.32	103.65
1368	5.369×10^{-7}	59.19	103.76
1381	7.016×10^{-7}	45.71	103.88
1390	1.004×10^{-6}	32.17	103.53
1403	1.251×10^{-6}	26.02	103.73
1377	6.095×10^{-7}	52.54	103.98

Table II. (Cont.)

Temp (°K)	Pressure (atm)	Mean free path/Diameter	$\Delta H^{\circ}298.15$ (kcal/mole)
0.34 cm diameter orifice			
1359	4.346×10^{-7}	54.76	103.62
1345	2.764×10^{-7}	65.42	103.83
1343	2.643×10^{-7}	89.17	103.81
1360	4.434×10^{-7}	53.81	103.66
1376	6.821×10^{-7}	35.37	103.61

Table III. Torsion-Langmuir Data for LaF_3

Orifice Diameter	Temp (°K)	Pressure (atm)	Evaporation Coefficient
1mm	1464	6.438×10^{-6}	1.12
	1471	6.438×10^{-6}	.96
	1544	3.540×10^{-5}	1.07
	1542	3.559×10^{-5}	1.13
	1573	7.121×10^{-5}	1.07
2mm	1437	2.528×10^{-6}	.84
	1504	1.510×10^{-5}	1.07
	1524	2.184×10^{-5}	.98
	1520	1.751×10^{-5}	.87
	1497	1.226×10^{-5}	1.00
	1472	6.834×10^{-6}	.97
	1455	3.321×10^{-6}	.71
	1432	2.249×10^{-6}	.83
	1416	1.551×10^{-6}	.85
	1474	6.224×10^{-6}	.84
3mm	1378	6.779×10^{-7}	1.01
	1398	1.070×10^{-6}	.70
	1428	2.245×10^{-6}	1.01
	1464	6.191×10^{-6}	1.08
	1432	2.530×10^{-6}	.93
	1390	8.073×10^{-7}	.85

Table IV. Calculated free energy functions for LaF_3

Temp (°K)	$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_s$ (cal/deg/mole)	$-\left(\frac{F^\circ_T - H_{298}}{T}\right)_g$ (cal/deg/mole)	$-\left(\frac{\Delta F^\circ_T - \Delta H_{298}}{T}\right)_{sub}$ (cal/deg/mole)
1000	38.972	87.411	48.439
1100	40.797	88.977	48.180
1200	42.355	90.073	47.718
1300	43.950	91.307	47.357
1400	45.486	92.475	46.989
1500	46.969	93.588	46.619
1600	48.400	94.650	46.250
1700	49.784	95.569	45.875
1800	51.129	96.622	45.493