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VAPORIZATION STUDIES OF LANTHANUM FLUORIDE

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(M.S. Thesis)

January 26, 1966

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ABSTRACT

The sublimation pressure of lanthanum fluoride was measured in the temperature range 1325° to 1650°K by the torsion-effusion method. The pressure data are represented by the expression

$$\log_{10} P_{\text{atm}} = -(2.174 \pm 0.009) \times \frac{10^4}{T} + 9.608 \pm 0.065$$

where the quoted errors are standard deviations from the least squares fit. The heat of sublimation at 298.15°K was found to be 107.45 ± 4 kcal/mole by the Second-Law method and 103.48 ± 4 kcal/mole by the Third-Law method. Assigning equal weights for the two methods, the heat of sublimation is taken as the average, 109.5 ± 5 kcal/mole.

I. INTRODUCTION

The importance of rare earth fluorides has increased significantly in recent years. Lanthanum fluoride currently plays an important role in the precipitation of fission product poisons. It is also a coprecipitant in a method for the determination of plutonium 239. Other uses include maser applications, laser applications and fluxes for titanium alloy welds.

Thermodynamic data for lanthanum fluoride have not been available. This paper reports measurements of the vapor pressure of lanthanum fluoride in the temperature range from 1325° to 1650°K as determined by the torsion-effusion method.^{1,2} The heat of sublimation at 298.15°K was calculated from the measurements by the Second and Third Law methods.

II. EXPERIMENTAL

A graphite cell with two eccentrically placed orifices was suspended in a furnace by a tungsten fiber. Vapor effusing out of the orifices caused a torque on the cell and the angles of cell rotation were recorded for various temperatures. Calculations of the pressure from the angle of twist were made from the relationship

$$P = \frac{2\theta D}{\sum q_i a_i f_i} \quad (a)$$

where D is the torsion constant of the suspending fiber, θ is the angle of cell rotation, a_i is the area of orifice i , q_i is the distance from the center of orifice i to the axis of cell rotation, and f_i is the Freeman-Searcy correction factor³ for the finite channel length of the orifice.

A detailed description of the furnace, auxiliary equipment and experimental techniques will not be given here. Similar equipment and techniques have been thoroughly discussed in a number of publications.^{4,10,24} It is sufficient to say that the cells were heated in a resistance furnace by radiation from tungsten hairpin shaped elements, and that one basic difference between the equipment for this research and that of previous studies lay in the use of a non-magnetic stainless steel column to enclose the suspension system instead of the commonly used Pyrex column. This change reduced the care necessary in handling the column and eliminated the danger of breakage.

The torsion cell consisted of a cell block, two cylindrical cells, and two cell end plates, all of graphite. The cells fit snugly into

holes in the side faces of the cell block. The cell end plates had orifices drilled through the centers through which vapor escaped.

The torsion cell was suspended by a tungsten fiber of approximately 5×10^{-3} cm in diameter and 43 cm in length. The torsion constant of the wire, D , was determined by measuring the periods of rotational oscillation of suspended masses of known moments of inertia. Then D was determined from the expression

$$D = \frac{4\pi^2(I_1 - I_2)}{t_2^2 - t_1^2} \quad (b)$$

where I_1 and I_2 are known moments of inertia of two different masses suspended from the fiber, and t_1 and t_2 are the periods of oscillation for the corresponding masses.

As the cell rotated in one direction due to the torque exerted by the escaping gases, it was manually rotated back to its original position by twisting the upper point of attachment of the fiber in the opposite direction. The restoring force was exerted and its angle was measured by means of a modified goniometer. The angles of twist were recorded to the nearest five-thousandths of a degree.

A black body hole was drilled into the bottom of the cell block upon which an optical pyrometer was focused. Temperature uniformity of the cell was assumed because (1) the cell was suspended in the central portion of a 8 cm vertical zone for which the temperature had been demonstrated to be constant to within 2°C and (2) measuring the surface temperature across the bottom of the cell showed no differences in

temperatures from one end of the cell to the other.

Although the optical pyrometer was calibrated by the D.C. Standards Laboratory of the Lawrence Radiation Laboratory, a discrepancy was noticed between the low-scale and the high-scale. Temperature readings at the same voltage setting yielded different results on the two scales. This discrepancy prompted a comparison between optically read temperatures and thermocouple measurements of the same temperature. A graphite calibration cell was constructed which allowed the thermocouple placement to be within 0.6 cm of the black body hole.

Both scales deviated systematically from the thermocouple readings. While the low scale deviated by 0° at 1025°C and 10° at 1225°C , the high scale deviated by only 1° at 1310°C and 7° at 1375°C . No deviations were noticed between 1200° and 1300°C on the high scale. The thermocouple temperatures and therefore all optical measurements were corrected accordingly.

It should be noted that the errors in the uncorrected pyrometer readings did not exceed the error limits claimed by the Leeds Northrup Company, yet because the errors were systematic they can produce a relatively large error in determinations of the 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 3.0%.

The validity of the calibrations was checked by measuring the vapor pressure of tin. Thirty tin datum points yielded an average third law heat of sublimation of 71.96 kcal/mole, which is in good

agreement with the values of 71.8 and 72.2 reported by Schulz⁴ and Hultgren.⁵

Prior to each series of lanthanum fluoride runs, the cell was checked for possible leakage. Lanthanum fluoride was loaded into a pair of cells which had no orifices. The cell was then heated to 1600°K and absence of significant leakage was demonstrated by absence of rotational deflections. Upon completion of the leakage test, orifices were drilled into the cell end plates.

The background pressure for all measurements was between 1.5×10^{-9} and 7.0×10^{-9} atm. The low background pressures made it possible to extend the range of reliable data well below 10^{-6} atm.

Each run started with a very slow increase in temperature from room temperature to 1650°K. Slow heating prevented violent cell block rotations and vibrations due to the outgassing of the assembly and dehydration of the sample. The furnace was held at 1650°K for one hour to eliminate volatile impurities. Data were then collected by making either random temperature changes of about 40° or by making smaller successive temperature changes in one direction on the temperature scale.

Various orifice sizes were used for this research. The orifice dimensions are given in Table I. To reduce the possibility of a systematic error, the suspending wire was replaced twice. The torsion constants of the wires were 2.1443, 2.0623, and 1.9787 dyne-cm/rad.

Table I. Orifice dimensions

| Cell | Orifice diameter (cm) | | Channel length (cm) | | Channel factor | |
|------|--------------------------|--------|------------------------|--------|----------------|--------|
| | (a) | (b) | (a) | (b) | (a) | (b) |
| 1 | 0.0990 | 0.0986 | 0.1499 | 0.1524 | 0.4697 | 0.4645 |
| 2 | 0.1594 | 0.1524 | 0.1633 | 0.1591 | 0.5508 | 0.5621 |
| 3 | 0.1866 | 0.1940 | 0.1628 | 0.1631 | 0.6063 | 0.6155 |
| 4 | 0.2633 | 0.2634 | 0.1506 | 0.1491 | 0.7043 | 0.7067 |
| 5 | 0.3452 | 0.3529 | 0.1613 | 0.1621 | 0.7465 | 0.7500 |

III. RESULTS AND DISCUSSION

The results of 110 vapor pressure determinations collected in the range 1325° to 1650°K are presented in Table II and Fig. 1. Below 1325°K, data were rejected because background sources of deflections were comparable with the deflections produced by effusion. A least squares fit on a pressure versus temperature plot yielded the following equation:

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

where the errors are standard deviations.

The vapor was assumed to consist only of LaF_3 molecules. Approximated 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 $\text{H}_2\text{O}(g)$ 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 heating hydrated rare earth fluorides in vacuum at temperatures of 1300° to 1600°K for an hour results in completely anhydrous samples.^{6,7}

The ratio of the mean free path to the orifice diameter, λ/d , was calculated at all readings by means of a hard sphere approximation⁸ with the sphere radius taken as the sum of the experimental La-F distance⁹ and the fluoride ion radius. It has been shown that too low a λ/d ratio implies that inapplicability of molecular flow equations.^{10,11} Measured pressures have been shown to deviate upward from the equilibrium

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

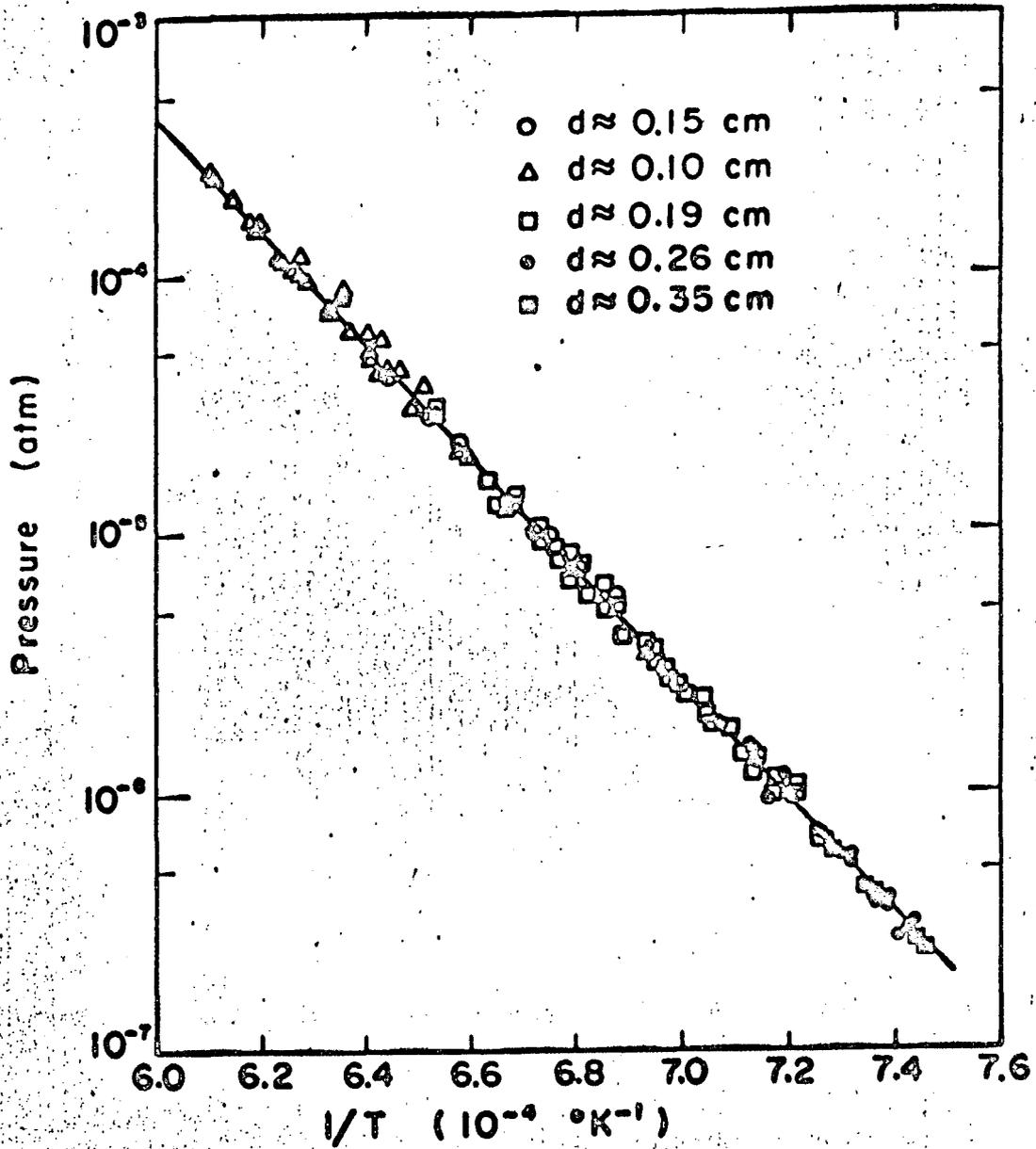
| Temp (°K) | Pressure (atm) | λ/d | $\Delta H^\circ_{298.15}$ (kcal/mole) |
|---------------------------------|------------------------|-------------|--|
| <u>0.10 cm diameter orifice</u> | | | |
| 1540 | 3.683×10^{-5} | 2.58 | 102.81 |
| 1559 | 5.484×10^{-5} | 1.76 | 102.86 |
| 1582 | 8.915×10^{-5} | 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 |
| <u>0.15 cm diameter orifice</u> | | | |
| 1523 | 2.177×10^{-5} | 2.83 | 103.35 |
| 1536 | 2.858×10^{-5} | 2.18 | 103.34 |

Table II. (cont.)

| Temp (°K) | Pressure (atm) | λ/d | $\Delta H^\circ_{298.15}$ (kcal/mole) |
|---------------------------------|------------------------|-------------|--|
| 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 |
| <u>0.19 cm diameter orifice</u> | | | |
| 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 | 1.627×10^{-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 |
| 1496 | 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 |
| 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^{-5} | 44.60 | 103.38 |
| 1394 | 1.173×10^{-6} | 38.22 | 103.37 |
| 1423 | 2.032×10^{-6} | 22.51 | 103.85 |

Table II. (cont.)

| Temp (°K) | Pressure (atm) | λ/d | $\Delta H^{\circ}_{298.16}$ (kcal/mole) |
|---------------------------------|------------------------|-------------|--|
| 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 |
| <u>0.34 cm diameter orifice</u> | | | |
| 1359 | 4.346×10^{-7} | 54.76 | 103.62 |
| 1345 | 2.764×10^{-7} | 85.42 | 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 |



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Fig. 1. Vapor pressure of lanthanum fluoride

pressure when the λ/d ratio is too low. Although no extensive quantitative work has been done on this problem a lower limit for λ/d near 1 has been found by Schulz.¹⁰ This research, in which the lower limit of λ/d was 0.40, showed no indications of a significant change in flow characteristics. The average heat of sublimation for all data with λ/d less than unity was within 0.5% of the heat of sublimation averaged over data with λ/d greater than unity.

The heat of sublimation was calculated by the Second-Law and Third-Law methods. The Third-Law requires combining free energy functions and pressure values at the same temperatures into the following equation:

$$\Delta H_{298.15}^{\circ} = -RT \ln P - T \left[\frac{\Delta F_T - \Delta H_{298.15}^{\circ}}{T} \right] \quad (d)$$

The Second-Law method utilizes the equation:

$$\Delta G = -R \ln P + a \ln T + 1/2 \Delta b T = 1/2 \Delta c T^{-2} = \frac{\Delta H_I}{T} + I \quad (e)$$

ΔH_I and I are constants from which the heats and entropy of sublimation are calculated, and a , b and c are constants of the empirical heat capacity equation $C_p = a + bT - cT^{-2}$.

The heat capacity of crystalline lanthanum fluoride was estimated by assuming a close relationship between cerium and lanthanum compounds. The difference between the heat capacities of La_2O_3 and $2(\text{LaF}_3)$ was taken as the difference between the heat capacities of Ce_2O_3 and $2(\text{CeF}_3)$. King and Christensen¹² reported $C_p = 17.9 + 10.14 \times 10^{-2}T + 1.10 \times 10^5 T^{-2}$ for $\text{CeF}_3(s)$. Kuznetsov and Rezhukhina¹³ found $C_p = 25.17 + 6.37 \times 10^{-3}T$ for Ce_2O_3 . Blomoeke and Zeigler¹⁴ found $C_p = 28.86 + 3.68 \times 10^{-3}T -$

$3.28 \times 10^5 T^{-2}$ for La_2O_3 . The heat capacity of $\text{LaF}_3(\text{s})$ was then estimated to be $C_p = 19.767 + 8.482 \times 10^{-3} T - 5.904 \times 10^{-4} T^2$. As expected, the heat capacity curve closely resembled that of CeF_3 .

The gaseous heat capacity was also estimated. Experimentally, it has been found that the La-F valence vibration in crystalline LaF_3 is 403 cm^{-1} .⁷ The La-F(g) stretch frequency was estimated on the assumption that the ratio of the valence vibration frequency in the crystalline state to the stretch frequency in the gaseous state is constant for similar molecules of the same point group. The Al-F valence vibration frequency in crystalline AlF_3 is 615 cm^{-1} and the Al-F stretching frequency in $\text{AlF}_3(\text{g})$ is 640 cm^{-1} .¹⁵ The La-F stretching frequency in $\text{LaF}_3(\text{g})$ was therefore estimated to be 419 cm^{-1} , which yields a stretching force constant of $1.96 \times 10^5 \text{ dyne/cm}$.

The validity of this approximation was substantiated by Lim.¹⁶ Using this approximation, he obtained a Ce-F stretching force constant of $2.04 \times 10^5 \text{ dyne/cm}$ in $\text{CeF}_3(\text{g})$ molecule. This constant was then compared with that calculated from an empirical equation formulated by Herschbach and Laurie.¹⁷ The two constants were within 10% of each other.

Plots of the out-of-plane bend force constant $\ln(k_2/l^2)$ and the in-plane bend force constant $\ln(k_3/l^2)$, where l is the La-F distance, versus k_1 for the constants of D_{3h} point group species¹⁸ showed a straight line relationship. k_2/l^2 and k_3/l^2 for LaF_3 were assumed to fall on this line. These force constants were thus estimated to be 0.192×10^5 and $0.103 \times 10^5 \text{ dyne/cm}$. Using the three force constants and the valence-force model,¹⁸ the following vibrational frequencies

for $\text{LaF}_3(\text{g})$ were calculated: 419, 156, 461(2) and 179(2) cm^{-1} .

The electronic contribution to the heat capacity was estimated by assuming that contributions were due to the La^{+3} ion only. Brewer et al.¹⁹ have shown that neglecting the presence of the halide ions and treating only the metal ion yields good thermodynamic estimates when applied to transition metal dihalides. Yashevitch²⁰ has found the electronic spectrum of La^{+3} to consist of a $^2\text{D}_{3/2}$, 0 cm^{-1} ground state and a $^2\text{D}_{5/2}$, 1603.23 cm^{-1} first excited level. All other energy levels are significant only at temperatures much higher than the temperatures of this research. Heat capacities for the gas were calculated at 100° intervals from 300° to 1800°K. The equation, $C_p = 21.424 - 4.065 \times 10^{-4} T - 3.375 \times 10^{-5} T^2$ was fitted to the values.

The free energy functions for the crystalline state were calculated using $C_p = 19.767 + 8.482 \times 10^{-3} T - 5.909 \times 10^{-4} T^2$ and Glassner's²¹ estimate of $S_{298.15}^\circ = 27.0$ eu/mole. Glassner's entropy estimate for $\text{CeF}_3(\text{s})$ was found to be 0.04 eu below the experimental value found by Westrum and Beale.²² The probable error in the estimate for S_{298}° , 0.2 eu, could cause 0.3 kcal/mole error in the heat of sublimation.

The estimated free energy functions for lanthanum fluoride between 1000° and 1800°K are given in Table III.

The heat of sublimation was calculated from each pressure measurement from Eq. (d). Values of $(\Delta F_T^\circ - \Delta H_{298.15}^\circ)/T$ at various temperatures were read to ± 0.01 cal from a curve drawn through the calculated values. 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

Table III. Calculated free energy functions for LaF_3

| Temp (°K) | $-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_s$ (cal/deg/mole) | $-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_g$ (cal/deg/mole) | $-\left(\frac{\Delta F_T^\circ - \Delta H_{298}^\circ}{T}\right)_{\text{sub}}$ (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 |

the mean.

A least squares calculation gave $\Sigma = (106.424 \pm 0.4400) \times 10^3/T - 43.291 \pm 0.302$, from which $\Delta H_{298.15}^{\circ} = 107.45 \pm 0.44$ kcal/mole and $\Delta S_{298.15}^{\circ} = 53.24 \pm 0.30$ eu were obtained.

The major sources of error in calculated heats of sublimation were the estimations of the heat capacities and free energy functions of the gas and solid. 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 solid free energy function. Errors in calibrating the wire, measuring the orifice diameter, channel length, and axis arms, and reading the angles of deflection cause an error of about 0.5% of the ΔH_{298}° . The temperature was assumed to be correct to within $\pm 5^{\circ}$. The pyrometer calibration presumably eliminated all temperature errors with the exception of the errors in the personal judgement of the brightness of the filament. An error of $\pm 5^{\circ}$ causes an error of $\pm 0.5\%$ 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 small 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. A $\pm 5^{\circ}$ systematic error in temperature causes an error of ± 3 kcal in ΔH_{298}° . The Second law heat of sublimation is therefore estimated to be accurate 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 energies and in the temperature dependence of the pressure measurements. Equal weights must be given to both values until accurate experimental data for the free energy functions of the gaseous and solid states become available. Therefore, the heat of sublimation at 298.15°K is fixed as 105.5 ± 5 kcal/mole. When more precise supporting thermochemical data become available, the Third-Law heat can be calculated with higher reliability.

At about the time these measurements were completed, a report of a vaporization study for lanthanum fluoride by Kent, Zmbov, Kana'an, Besenbruch, McDonald and Margrave²⁵ became available. They had measured the sublimation pressures of lanthanum fluoride by mass spectrometric and semi-microbalance studies via the Langmuir technique. The mass spectrometer values were calibrated by combining the least square equations of $\log P_{wt \text{ loss}}$ and $\log (I^+T)$ versus $1/T$ to obtain a value for the machine constant k of the equation $P = kI^+T$. The pressure obtained lie about a factor of 2 below the data reported in this paper. Identical trends were noted when Margrave's data for CaF_2 ²³ and BaF_2 ²⁴ were compared with those of Schulz¹⁰ and Hart²⁴ 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.

The physical appearance of the sample changed markedly upon heating.

The originally flaky, white powder had changed to a dense consolidated grey mass. Heating to temperatures above 1500°K for times of two hours or more caused small crystals to form in the mass. Evidently the increased temperatures produced an increase in ordering of the complex hexagonal crystal structure by facilitating the mobility of defects. Similar physical effects were observed by Lim¹⁶ and Batsanova et al.⁷

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