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Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

VAPOR PRESSURE AND HEAT OF SUBLIMATION
OF CALCIUM FLUORIDE

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ABSTRACT

The vapor pressure of CaF_2 was investigated in the temperature range 1400 to 1850°K by the torsion-effusion method. Molecular-streaming conditions were demonstrated to break down when the mean free path became about as short as the orifice diameter, but a dependence on orifice channel length was observed. The vapor pressure (in atmospheres) of $\beta\text{-CaF}_2$ is given by the equation

$$\log P = -19,973/T + 7.8717$$

in the experimental range. Extrapolation yields a calculated normal boiling point of 2786°K and a heat of sublimation at 298°K of 101.2 kcal by the third-law method and 101.4 kcal by the second-law method.

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INTRODUCTION

The only vapor-pressure measurements that have been available for calcium fluoride were obtained by Ruff and Le Boucher by use of a dynamic method.³ Their method entailed observation of the temperature at which a substance begins to boil when under an experimentally fixed ambient pressure and could be applied only for determination of vapor pressures of liquids. The lowest temperature of measurement by Ruff and Le Boucher was 2086°K.

It seemed desirable to measure the vapor pressure of CaF_2 at lower temperatures in order to check the reported pressures and obtain a value for the heat of sublimation at 298°K from data that required less extrapolation. The torsion-effusion method was applied in the research reported here.^{4, 5}

EXPERIMENTAL PROCEDURE

In the torsion-effusion method, an effusion cell is suspended in a vacuum furnace by a fine wire. Upon heating, vapor escapes through eccentrically placed orifices in the cell, thereby 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 formula $P = 2\phi D / (\Sigma q a^2)$, where P is the vapor pressure, D is the torsion constant of the wire, q is the perpendicular distance from the cell center to the axis of the effusion hole,

a is the area of the orifice, f is the force-reduction factor due to finite orifice-channel length, and ϕ is the angle through which the cell has rotated. Values for f have been tabulated by Freeman and Searcy,⁶ Detkov,⁷ and Schulz and Searcy.⁸

For this research, the suspension thread was 17 in. of 2-mil-diam. tungsten wire. Components of the effusion cell and cell block were of National Carbon AUC premium graphite. Four chambers with axes $7/16$ in. from the center of the cell block were drilled, into the side of the block, two each on opposing faces. Two loaded effusion cells with effusion orifices oriented to yield additive torques were fitted into two of the four chambers of the cell block. Empty cells were fitted into the other two chambers. In other runs the positions of the effusion cells and of the empty cells were reversed in order to evaluate and subtract the influence of a residual torque that resulted from electromagnetic repulsion of the torsion assembly by the alternating field of the furnace element.⁹

The calcium fluoride used in this work was supplied by Dr. K. K. Kelley of the U. S. Bureau of Mines and was from the same lot as that on which Naylor performed heat-content experiments.¹⁰

Two sets of lids were used. One set had orifices that were $1/16$ in. in diameter and $1/32$ in. thick, and the other had orifices $1/4$ in. in diameter and $1/32$ in. thick. The cell block, crucibles, and lids were degassed at 1900°C . Samples were heated in cells whose lids contained no holes, in order to check for torque produced by sample leakage. None was found.

In a typical run, about 1 g of calcium 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 selected pair of holes in the cell block.

Counter cells, containing no sample, were placed in the remaining pair of holes. In making a run, the power was turned on and gradually raised, while the ambient pressure was kept below 5×10^{-5} mm, until a deflection of about 1 radian was noted on the circular scale. The cell was allowed to remain at this power setting for about an hour; then the deflection and temperature were recorded. The temperature was lowered in steps of 10 to 20°C, and allowed to equilibrate at each temperature for 20 min. Deflection and temperature readings were taken, the temperature was again lowered 10 to 20°C, and the procedure repeated until the deflection became too small to measure. After the system had reached room temperature, the zero-point position was noted.

To obtain corrections for the residual deflection, runs were made in which the effusion holes were placed to reverse the direction of torque. With this arrangement, the residual deflection became subtractive. The two orientations of effusion holes yielded pairs of flaring deflection vs $1/T$ curves, very close together at high pressures and parting at lower ones. Smooth curves were drawn through both sets of points. For every data point in each set, an isothermal line was drawn intersecting the smoothed curve through the other set. The data points of each curve were then averaged with the intercepts of the smoothed curve with the other curve to obtain corrected deflections. These corrected deflections were then converted into pressures. These pressures, corrected for thermal expansion of the cell parameters, are shown in Table I and Fig. 1.

A more detailed description of the apparatus and techniques is given in a previous paper.⁹

RESULTS AND DISCUSSION

Studies on low-pressure gas flow have demonstrated that the molecular flow equations become inapplicable when the mean free path of the vapor approximately equals the diameter of the effusion orifice. Table I, therefore, shows for each measurement the calculated ratios λ/d of the mean free path to the average orifice diameter in addition to the pressure and the third-law value of the heat of sublimation at 298°K. Orifice dimensions for each cell are listed in Table II. These ratios were calculated by using the hard-sphere approximation, with the molecular diameter of CaF_2 taken as 7.4 Å, the sum of ionic diameter at room temperature. The numerical values of λ/d calculated by this approximation cannot be quantitatively correct, but they are satisfactory for internal comparisons.

In Fig. 1, circles indicate those points with calculated λ/d ratios less than unity; those with ratios greater than unity are shown as dots. The solid line of the graph is calculated from heats of sublimation obtained from the low-temperature data. As can be seen from this graph, when the larger orifice was used, molecular flow prevailed to just the temperature for which λ/d is calculated to be unity. When the smaller orifice was used, molecular flow prevailed to a temperature for which λ/d is calculated to be about 0.3.

For $\beta\text{-CaF}_2$ the vapor pressure in atmospheres is given by the expression $\log P = -19,973/T + 7.8717$. The heat of sublimation of $\alpha\text{-CaF}_2$ at 298°K was calculated from the lower-temperature data for each orifice by both the second-law (sigma-plot) method and the third-law method. For the sigma-plot method the equation

$$\Sigma = -R \ln p + Aa \ln T + 1/2 Ab T = \frac{\Delta H_1^0}{T} + I$$

was used. In this equation ΔH_1^0 and I are constants from which the heat and entropies of sublimation can be calculated, and a and b are the constants in

the heat-capacity equation $C_p = a + bT$.

For β -CaF₂ Kelley¹² reports that $C_p = 25.81 + 2.50 \times 10^{-3} T$ ($\pm 0.1\%$) in the range from 1424 to 1691°K. Brewer et al.¹³ has estimated the vibration frequencies for gaseous CaF₂ to be 484, 95(2), and 675 cm⁻¹. Heat capacities were calculated from these frequencies at 50° intervals.

The least-squares calculation yields $Z = (111,615)/T - 133.27$, from which $\Delta H_1^\circ = 111,615$, and $\Delta H_{1543}^\circ = 91.50$ kcal. This compares with $\Delta H_{1543}^\circ = 91.39$, which is calculated from the assumption that $\Delta C_p = 0$ in the experimental range. Graphical integration of the heat capacities from 298 to 1543°K yields 17.99 kcal. The difference in heat content between α -CaF₂ at 298° and β -CaF₂ at 1543° is 27.93 kcal.¹² Therefore, ΔH_{298}° for sublimation of α -CaF₂ is calculated to be 101.44 kcal.

Free-energy functions for the third-law calculations were available for the gas at 500° intervals,¹³ and heat-content and entropy data were available for the solid at 100° intervals.¹² Kelley and King list 16.46 ± 0.03 e.u. as the entropy of α -CaF₂ at 298°K.¹⁴ Free-energy functions were plotted for the condensed phases and the gas, and smooth curves were drawn through each set. Free-energy functions read from the curves were combined with the individual pressure values in the equation $\Delta H_{298}^\circ = -RT \ln p - T \frac{\Delta F_{298}^\circ - \Delta F_{298}^\circ}{T}$ to yield ΔH_{298}° values. The average third-law ΔH_{298}° value with standard deviation from the 11 lowest-temperature vapor-pressure points obtained with the small effusion holes is 101.22 ± 0.02 kcal. The average from 23 points when a hole 16 times greater in area was used is 101.14 ± 0.02 kcal. The apparent error is therefore ± 0.06 kcal between the two sets or the average ΔH_{298}° is 101.17 ± 0.06 kcal. The sum of the errors made in measuring orifice areas, lid thicknesses, moment arms, and torsion constants should not contribute more than a 2% error in the calculated vapor pressures. Deflection

were read to the nearest 0.001 radian and therefore contribute possible errors of 0.1% at the higher deflections and 10% for 0.01 radian deflections. Pressure errors should then vary from 2 to 12%, depending upon the magnitude of the deflection. Black-body conditions for temperature measurement were established by use of several holes of varied depths. No dependence of measured temperature on hole depth was found. The National Bureau of Standards certifies the corrected table of temperatures for the pyrometer used to be accurate to within $\pm 3^\circ$ in the temperature range investigated. An error of about $\pm 3^\circ$ arises from the problem of matching brightness in our experiments. Since the $\pm 3^\circ$ calibration uncertainty arises largely from the same problem of matching brightnesses, a total error of $\pm 5^\circ$ in temperature is estimated.

The pressure and temperature errors could therefore amount to uncertainties of 0.4% in the ΔH_{298}° values obtained from large deflections and 0.7% in values from smallest deflections used. Other errors to be considered are those contained in the free-energy functions. If all estimated errors are taken into account, a gross uncertainty of 1 kcal is estimated for the heat of sublimation at 298°K.

From the third-law average value $\Delta H_{298}^\circ = 101.17 \pm 1.5$, the heat of sublimation of $\beta\text{-CaF}_2$ at its melting point is calculated to be 99.01 kcal.

Extrapolation with heat-capacity data for the liquid and gas yields calculated vapor pressures in the liquid range. The normal boiling point and heat of vaporization at the boiling point are calculated to be 2786°K and 78.0 kcal. In Fig. 1, the liquid pressure curve calculated from the third-law data is seen to be in good agreement with experimental points of Ruff and Le Beauher.³ The low-temperature data extrapolated over 300°C from below the melting

point yield pressure values higher by less than 10% than those of Ruff and Le Boucher.

In these calculations it is assumed that $\text{CaF}_2(\text{g})$ was the vaporizing species. The only gaseous calcium fluoride molecule yet observed spectroscopically is $\text{CaF}(\text{g})$.¹⁵ However, thermodynamic calculations show that the total pressure to be expected from the reaction $\text{CaF}_2(\text{l}) \rightarrow \text{CaF}(\text{g}) + \text{F}(\text{g})$ would be at least several orders of magnitude below the observed pressures. Calculations also demonstrate that dissociation to elemental calcium and fluorine gas is negligible. Hammer found magnesium fluoride vapor to have the molecular weight of MgF_2 monomer molecules.¹⁶ Calcium fluoride was expected, therefore, to evaporate primarily to CaF_2 monomer molecules. The excellent agreement between heats of sublimation calculated by the second- and third-law methods and between our extrapolated pressures and the measured pressures of Ruff and Le Boucher lend confidence to the conclusion that the correct evaporation reaction has been chosen.

ACKNOWLEDGMENTS

We gratefully acknowledge the valuable counsel of Dr. David J. Meschi in design and operation of the equipment.

FOOTNOTES AND REFERENCES

1. This work was done under the auspices of the U. S. Atomic Energy Commission.
2. From the thesis submitted by D. A. Schulz in partial fulfillment of the requirements of the Ph. D. degree.
3. O. Ruff and L. Le Boucher, *Z. anorg. u. allgem. Chem.* 219, 376 (1934).
4. H. Mayer, *Z. Physik* 67, 240 (1931).
5. M. Vollmer, *Z. Physik. Chem., Bodenstein Festband*, 863 (1931).
6. R. D. Freeman and A. W. Searcy, *J. Chem. Phys.* 22, 762 (1954).
7. S. P. Detkov, *Zhur. Fiz. Khim.* 34, 1631 (1960).
8. D. A. Schulz and A. W. Searcy, *J. Chem. Phys.*, in press.
9. A. W. Searcy and D. A. Schulz, submitted to *J. Chem. Phys.*
10. B. Naylor, *J. Am. Chem. Soc.* 67, 150 (1945).
11. S. Dushman, Scientific Foundations of Vacuum Technique (John Wiley & Sons, Inc., New York, 1949), Chap. 1.
12. K. K. Kelley, U. S. Bureau of Mines Bulletin 584, 39 (1960).
13. L. Brewer, G. Somayajulu, and H. Brachett, Lawrence Radiation Laboratory Report UCRL-9840, September 1961.
14. K. K. Kelley and E. G. King, U. S. Bureau of Mines Bulletin 592, (1961).
15. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules (D. Van Nostrand Co., New York, 1950.)
16. R. R. Hammer, The Vapor Pressure of Magnesium Fluoride, Ph. D. Thesis, University of California, September 1961.

Table I. Temperature, pressures, and ratios of mean free path to orifice diameter.

Temperature (°g.)	Pressure (atm)	λ/d	ΔH_{298}^0 (kcal)
1624	4.284×10^{-5}	0.63	100.77 ^a
1612	3.256×10^{-5}	0.83	100.98 ^a
1598	2.494×10^{-5}	1.07	101.03
1584	1.862×10^{-5}	1.42	101.15
1564	1.251×10^{-5}	2.09	101.25
1550	9.652×10^{-6}	2.69	101.23
1530	6.614×10^{-6}	3.87	101.16
1516	4.927×10^{-6}	5.15	101.22
1497	3.472×10^{-6}	7.23	101.06
1477	2.308×10^{-6}	10.73	101.04
1467	1.793×10^{-6}	13.72	101.12
1449	1.240×10^{-6}	19.61	101.08
1435	8.724×10^{-7}	27.61	101.21
1421	6.175×10^{-7}	38.64	101.25
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1630	4.804×10^{-5}	0.57	100.77 ^a
1616	3.570×10^{-5}	0.76	100.90 ^a
1610	3.063×10^{-5}	0.87	101.04 ^a
1592	2.174×10^{-5}	1.23	101.12
1576	1.605×10^{-5}	1.64	101.16
1556	1.087×10^{-5}	2.40	101.17
1541	8.336×10^{-6}	3.10	101.11
1518	5.366×10^{-6}	4.79	101.10
1505	3.937×10^{-6}	6.41	101.25
1484	2.670×10^{-6}	9.32	101.08
1470	1.984×10^{-6}	12.42	101.03
1456	1.475×10^{-6}	16.56	101.03
1442	1.017×10^{-6}	23.13	101.11
1427	7.009×10^{-7}	33.79	101.26
<hr/>			
1830	9.179×10^{-4}	0.13	100.20 ^a
1821	8.013×10^{-4}	0.15	100.50 ^a
1812	6.954×10^{-4}	0.16	100.51 ^a
1795	5.423×10^{-4}	0.22	100.74 ^a
1783	4.816×10^{-4}	0.25	100.86 ^a
1779	4.157×10^{-4}	0.29	100.96 ^a
1770	3.576×10^{-4}	0.33	101.05 ^a
1762	3.109×10^{-4}	0.38	101.17 ^a
1748	2.566×10^{-4}	0.46	101.17 ^a
1734	2.069×10^{-4}	0.55	101.27
1715	1.453×10^{-4}	0.80	101.51 ^a
1700	1.200×10^{-4}	0.96	101.51 ^a
1696	1.163×10^{-4}	0.98	101.39 ^a
<hr/>			
1679	9.163×10^{-5}	1.24	101.31
1663	7.750×10^{-5}	1.45	101.25
1656	6.337×10^{-5}	1.76	101.25
1640	4.881×10^{-5}	2.27	101.25

Table I. (cont'd.)

Temperature (°K)	Pressure (atm)	λ/d	ΔH_{298}° (kcal)
1845	1.185×10^{-3}	0.10	100.20 ^a
1833	1.003×10^{-3}	0.12	100.25 ^a
1820	8.204×10^{-4}	0.15	100.39 ^a
1805	6.434×10^{-4}	0.19	100.61 ^a
1795	5.415×10^{-4}	0.22	100.74 ^a
1781	4.313×10^{-4}	0.25	100.56 ^a
1765	3.252×10^{-4}	0.32	100.69 ^a
1753	2.714×10^{-4}	0.34	101.25 ^a
1739	2.224×10^{-4}	0.53	101.28 ^a
1729	1.897×10^{-4}	0.61	101.32 ^a
1721	1.575×10^{-4}	0.71	101.63 ^a
1711	1.359×10^{-4}	0.83	101.62 ^a
1689	1.054×10^{-4}	1.00	101.36
1676	8.747×10^{-5}	1.29	101.28
1664	7.181×10^{-5}	1.56	101.27
1649	5.814×10^{-5}	1.92	101.13
1634	4.540×10^{-5}	2.43	101.13
1625	3.803×10^{-5}	2.83	101.12
1611	3.106×10^{-5}	3.51	101.07

^a All heats bearing this symbol were calculated from experimental data for which the mean free path was less than the diameter of the effusion hole. These heats were not considered in the computation of the average therefore.

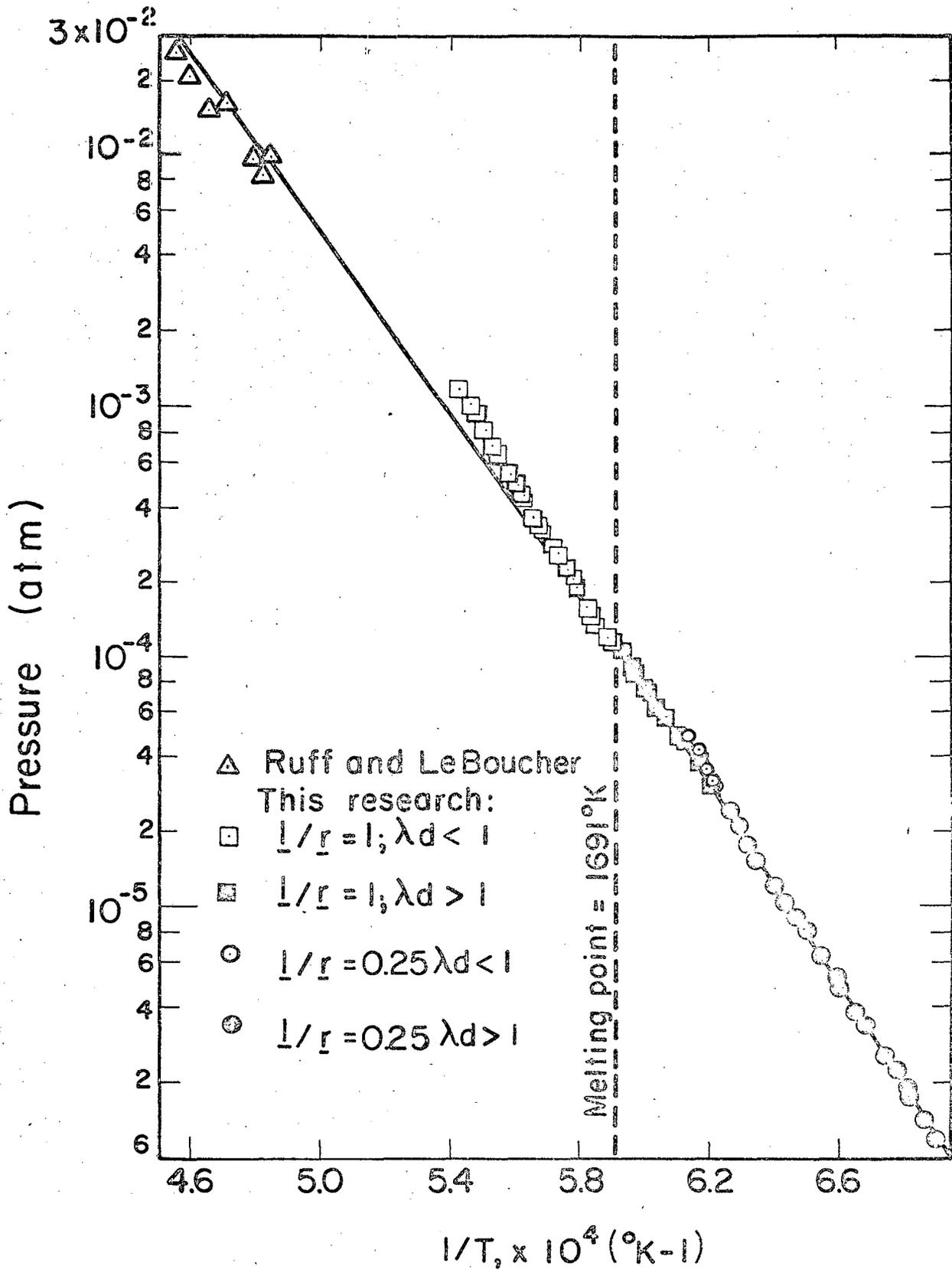
Table II. Orifice dimensions ^a

Cell	Hole diameter (cm)		Lid thickness (cm)		Channel factor		Moment arm (cm)	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1	0.32160	0.32314	0.03759	0.04064	0.92704	0.92171	0.8684	0.8700
2	0.32160	0.32314	0.03759	0.04064	0.92704	0.92171	0.8827	0.8827
3	0.07984	0.07939	0.04115	0.04064	0.72645	0.72783	0.8684	0.8700
4	0.07984	0.07939	0.04115	0.04064	0.72645	0.72783	0.8827	0.8827

^a The torsion constant for these runs was $1.9897 \text{ dyne-cm-rad.}^{-1}$

FIGURE LEGEND

Fig. 1. Vapor pressure of calcium fluoride.



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