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VAPOR PRESSURE AND HEAT OF SUBLIMATION OF BARIUM FLUORIDE

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Patrick E. Hart

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VAPOR PRESSURE AND HEAT OF SUBLIMATION OF BARIUM FLUORIDE

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January 16, 1964

ABSTRACT

The vapor pressure of barium fluoride was measured in the temperature range 1261 to 1548°K by the torsion-effusion method. The vapor pressure of barium fluoride in atmospheres is given by the expression

$$\log P = -\left(\frac{78.70}{45.76} \pm 1.42\right) \times \frac{10^4}{T} + 6.94 \pm 0.23$$

where the quoted errors are the standard deviation from the least-squares fit.. Extrapolation of the data yields a heat of sublimation at 298°K of 90.29 ±2 kcal/mole by the third-law method and 87.06 ±1.45 kcal/mole by the second-law method.

INTRODUCTION

Only limited vapor pressure data have been available for barium fluoride. Ruff and LeBoucher[1] obtained pressures between 1960 and 2206°K by use of a dynamic method. Blue et al.[2, 2a, 2b] used a mass spectrometer to obtain vapor pressure data by the Knudsen method at temperatures between 1232 and 1505°K.. A second-law heat of sublimation was determined directly from a plot of log $I^+ \times T$ vs $1/T$. The mass spectrometer pressures were normalized to agree with free-surface weight loss studies.[2b] The normalized pressures were used to calculate the heat of sublimation at 298°K by the third-law method. Pressures were calculated from the weight loss study by means of the Langmuir equation with the assumption that the sublimation coefficient was unity. The pressures calculated in the Langmuir study as well as the pressures calculated in the mass spectrometer study would be in error if the sublimation coefficient of barium fluoride is less than unity.

It seemed advantageous to measure pressures for barium fluoride in the temperature range of the Langmuir study by a method that clearly gives equilibrium data. Accordingly, the torsion-effusion method[3, 4] has been applied to determine the vapor pressure of barium fluoride in the temperature range from 1261 to 1548°K. This work extends the investigation of the alkaline earth dihalides by the torsion-effusion technique begun by Schulz and Searcy.[5]

EXPERIMENTAL

An effusion cell was suspended in a vacuum furnace from a fine fiber. The cell is so designed that vapor effuses from two eccentrically placed orifices in the cell walls creating a torsional force on the fiber. Unless a counter-torque is imposed, the cell will rotate through an angle φ which is related to the vapor pressure P of the material in the cell by the expression $P = \frac{2\varphi D}{\Sigma qaf}$ where D is the torsional constant of the suspension fiber, q is the distance from the orifice to the axis of rotation of the cell, a is the area of the orifice, and f is the factor that corrects for the finite channel length of the orifice.[6, 7]

In this research, the torque was balanced by the use of an electromagnetic field that acted on a very weak permanent magnet which was incorporated into the cell suspension system. About the glass torsion column of the system, two small solenoids were mounted diametrically opposed. A Power Design Model 5015A power supply was used to supply DC current to the solenoids wired in series. In series with the supply was a 30-ohm resistor which decreased the obtainable current to the required range of 600 to 0.1 ma.

As the cell rotated out of its null position during heating, the current supplied to the solenoids was adjusted by means of a vernier attachment to the power supply to return the cell to its original position. Vapor pressures are directly proportional to this current since the torque set up by a current flowing through a solenoid is directly proportional to the current.

The suspension system was calibrated for measurement of angular deflection by applying current to the electromagnets as the suspension was rotated a known number of degrees. The suspension fiber was a 2-mil diam tungsten fiber, 40 cm in length.

The cells made of National Carbon ZT101 grade graphite were of a "match box" shape about 3.0 cm in length, 1.3 cm in width, and 1.9 cm in height. Two different orifice diameters were used as shown in the appendix. One set was 0.20 cm in diam and the other 0.10 cm. Wall thickness at the orifice for both sets was 0.10 cm.

The furnace heating elements were of hairpin-shaped tungsten wires connected in series. Electromagnetic repulsion of the torsion assembly as noted in other torsion-effusion work[5] was not observed because of self-canceling of the induced field in the hairpin elements. Before effusion holes were machined in the cell walls, each cell with sample was tested for possible leakage. No observable deflection was found when the cell and sample were heated to 1450°K. Therefore, it was assumed that measure deflections during the experiment were due only to effusion of vapor through the machined orifices.

Temperatures were measured by a thermocouple placed in a dummy graphite cell located near the effusion cell in the furnace hot zone. To calibrate the cell, a thermocouple was mounted in an effusion cell and was calibrated by a gold point determination with the cell in the furnace in which the vapor pressure studies were made. A temperature correlation between dummy and effusion cell temperatures was obtained by measuring temperatures in both cells at a series of power settings. A maximum temperature difference between the two cells of 15 degrees was found at 1379°K with the dummy cell being at a lower temperature than the effusion cell.

For this research, barium fluroide of optical quality from Semi-Elements lot SE80060 was used. Prior to a run, the cell and sample were heated to some 50° higher than the highest temperature to be reached during the run and until the ambient pressure in the furnace was no higher than 5×10^{-5} mm. In any particular run from 2 to 6 points were taken with at least 15 min being allowed after each temperature change in order to insure that equilibrium was reached. The pressures obtained are shown in Fig. 1 and Table I.

For some runs, after long periods of heating at high temperatures, very rapid decreases in pressures were noted. These decreases indicated that the sample had been depleted and not enough remained to maintain an equilibrium pressure in the cell. The color of the residue changed from white to gray during these runs. Also the residue formed a very dence compact indicating that some side reaction had taken place.

Thermodynamic calculations indicate that the pressure produced by the reactions $BaF_2(s) + C(s) = BaF(g) + CF(g)$, $BaF_2(s) + C(s) = Ba(g) + CF_2(g)$, and $BaF_2(s) + \frac{1}{2} C(s) = BaF(g) + \frac{1}{2} CF_2(g)$ would be several orders of magnitude below the observed pressures. Furthermore, x-ray diffraction patterns of the samples after heating indicated that no change in structure had occurred. Therefore, the loss of cell material was apparent rather than real. It may be due to some surface effect such as graphite covering the surface of the sample and may not be caused by a reaction between the graphite and sample.

The decrease in pressures that resulted from the apparent depletion was extremely rapid and the start of the pressure reduction was easily identified. All those points taken before the decrease were included in calculations of the vapor pressure for barium fluoride.

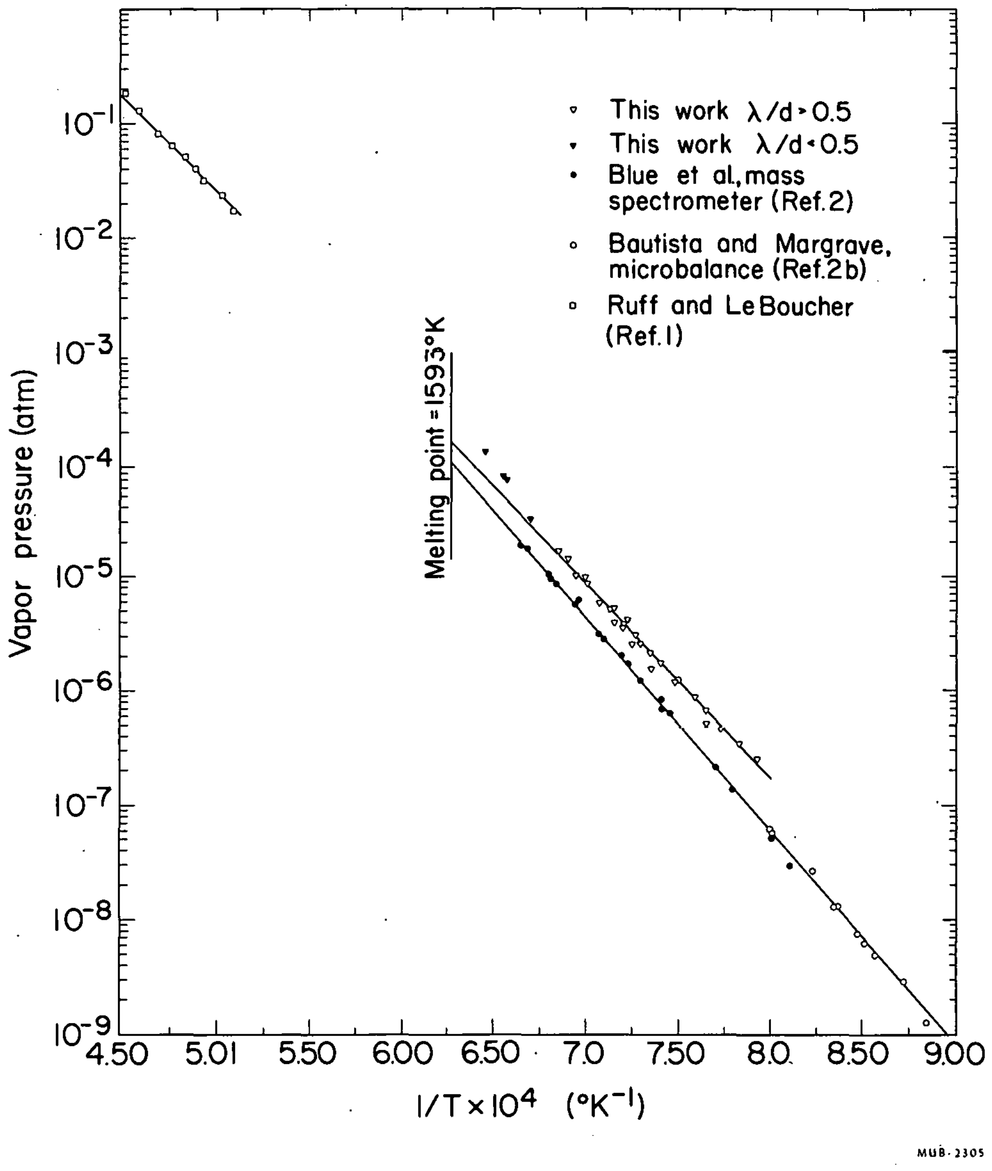

Fig. 1. Vapor pressure of barium fluoride.

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

Temp. (°K)	Pressure (atm)	λ/d	ΔH°_{298} (kcal/mole)
1491	3.320×10^{-5}	0.356	89.810
1459	1.688×10^{-5}	0.700	90.166*
1440	1.026×10^{-5}	1.152	90.572*
1414	5.828×10^{-6}	2.028	90.741*
1388	3.560×10^{-6}	3.283	90.612*
1548	1.236×10^{-4}	0.096	88.705
1520	6.900×10^{-5}	0.171	89.089
1358	1.585×10^{-6}	7.456	90.991*
1378	2.555×10^{-6}	4.625	90.922*
1395	3.954×10^{-6}	2.989	90.070*
1425	8.766×10^{-6}	1.348	90.205*
1358	2.182×10^{-6}	5.416	90.545*
1448	1.441×10^{-5}	0.821	90.034*
1526	7.554×10^{-5}	0.156	89.165
1401	5.272×10^{-6}	1.021	90.269*
1305	6.102×10^{-7}	8.818	90.215*
1430	9.902×10^{-6}	0.543	90.130*
1388	3.800×10^{-6}	1.416	90.458*
1402	5.219×10^{-6}	1.031	90.333*
1293	4.683×10^{-7}	11.490	90.125*
1308	6.758×10^{-7}	7.962	90.125*

Table I. (cont.)

Temp. (°K)	Pressure (atm)	λ/d	ΔH°_{298} (kcal/mole)
1318	8.698×10^{-7}	6.186	90.117*
1375	3.078×10^{-6}	1.748	90.245*
1359	2.134×10^{-6}	2.521	90.278*
1277	3.466×10^{-7}	1.553	89.876*
1261	2.516×10^{-7}	2.139	89.640*
1375	3.105×10^{-6}	1.733	90.219*
1384	4.202×10^{-6}	1.281	89.922*
1370	2.529×10^{-6}	2.128	90.477*
1350	1.732×10^{-6}	3.107	90.291*
1336	1.191×10^{-6}	4.518	90.431*

*Indicates heats where λ/d was calculated to be greater than 0.5

The first 14 points were taken with the small orifice.

The vapor pressure of tin was measured as shown in Fig. 2 and Table II to check for any systematic errors that would affect pressure readings. The third-law heat of sublimation at 298°K was determined in this work is $\Delta H^{\circ}_{298} = 71.92 \pm .27$ kcal/mole. By the torsion-effusion method, Schulz[8] found $\Delta H^{\circ}_{298} = 71.8$ kcal/mole as compared with $\Delta H^{\circ}_{298} = 72.2 \pm .50$ kcal/mole given by Hultgren et al.[9] Therefore, no systematic error was indicated in the present work.

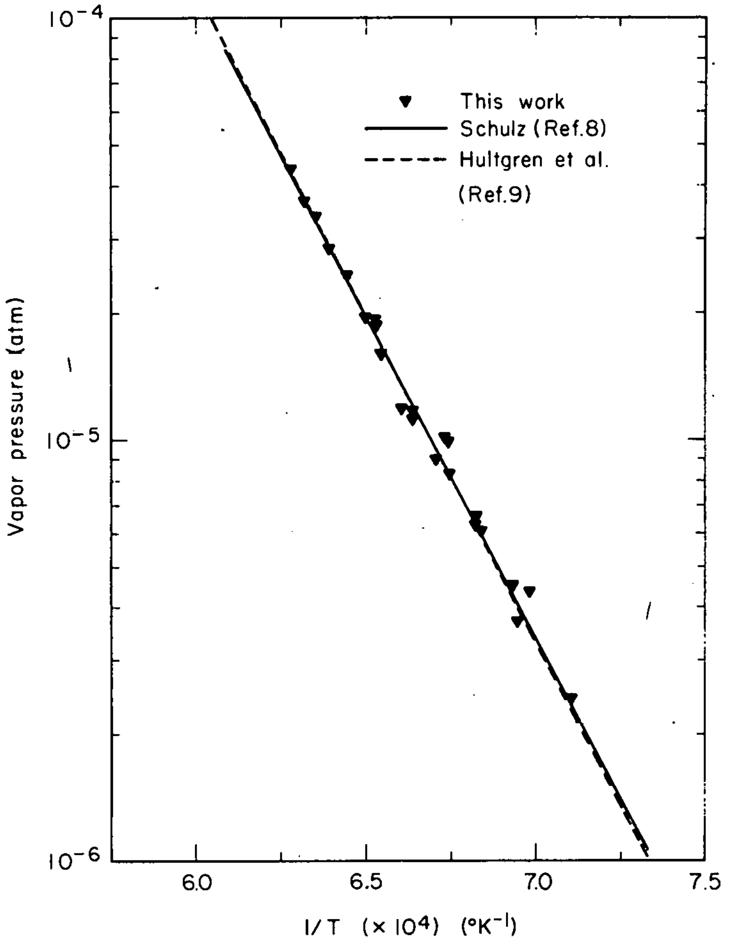

Fig. 2. Vapor pressure of tin (ℓ).

Table II. Temperature, and Pressures of Tin (ℓ).

Temp. (°K)	Pressure (atm)	ΔH°_{298} (kcal/mole)
1582	3.696×10^{-5}	72.061
1566	2.858×10^{-5}	72.151
1537	1.897×10^{-5}	72.097
1527	1.688×10^{-5}	71.985
1507	1.331×10^{-5}	71.767
1485	1.010×10^{-5}	71.565
1465	6.529×10^{-6}	71.882
1442	4.460×10^{-6}	71.864
1532	1.829×10^{-5}	71.975
1512	1.366×10^{-5}	71.930
1483	9.856×10^{-6}	71.536
1466	6.222×10^{-6}	72.072
1436	4.312×10^{-6}	71.671
1406	2.403×10^{-6}	71.829
1590	4.361×10^{-5}	71.902
1537	3.388×10^{-5}	71.022
1554	2.446×10^{-5}	72.089
1531	1.749×10^{-5}	72.061
1507	1.232×10^{-5}	72.003
1483	8.255×10^{-6}	72.058
1463	6.060×10^{-6}	71.998
1491	8.871×10^{-6}	72.229
1440	3.696×10^{-6}	72.305

RESULTS AND DISCUSSION

Molecular flow equations for low-pressure gas flow have been shown to apply only when the mean free path of the vapor species is greater than the diameter of the effusion orifice. Table II shows at each measurement the pressure and the thrid-law values of the heat of sublimation at 298°K in addition to the calculated ratio λ/d of the mean free path to the orifice diameter. These ratios were calculated by using the hard sphere approximation[10] with the molecular diameter of barium fluoride taken as 8.14Å. the sum of ionic diameters at room temperature, assuming a linear molecule. The value of λ/d can be used only for relative comparison.

Recent experiments[11] indicate barium fluoride is a bent molecule and thus would have a slightly smaller effective molecular diameter than assumed. Therefore, pressures for which λ/d is as low as 0.5 are included in the final calculation of ΔH°_{298}. This cut-off is an arbitrary selection; however, where λ/d was less than 0.5, ΔH°_{298} values at least 0.6 kcal/mole below the average were found using the smallest orifice.

A least-squares calculation for the data gives the vapor pressure of barium fluoride in atmospheres as $\log P = -\left(\frac{78.70}{45.76} \pm 1.42\right) \times \frac{10^4}{T} + 6.94 \pm 0.23$ between 1261 and 1548°K. The errors are the standard deviation from the least-squares fit. For each orifice diameter, the heat of sublimation of barium fluoride at 298°K by both the second-law (sigma plot) and third-law method are calculated. In all calculations BaF_2 gas is considered to be the major vapor species.[2a, 11] For the second-law method the equation

$$\Sigma = -R \ln P + \Delta a \ln T + \frac{\Delta b}{2} T - \frac{\Delta c}{2T^2} = \frac{\Delta H^\circ_I}{T} + I$$

was used, where a, b, and c are constants in the heat capacity equation $C_p = a + bT - \frac{c}{T^2}$ and H°_I is the constant from which the heat sublimation at 298°K can be calculated. Kelly[12] gives for $BaF_2(s)$ $C_p = 13.98 + 10.2 \times 10^{-3}$ T in the range of 298 to 1300°K. Brewer et al.[13] have estimated the vibrational frequencies to be 439, 70(2), and 496 cm^{-1} for $BaF_2(g)$. From these constants, heat capacities for the vapor phase were estimated at 100° intervals giving $C_p = 14.7 + 13.2 \times 10^{-3} T - \frac{0.109 \times 10^6}{T^2}$. Thus, the change in heat capacity during vaporization is $\Delta C_p = 0.72 - 10.07 \times 10^{-3} T - \frac{0.109 \times 10^6}{T^2}$. From a least-squares calculation for the second-law method, $\Delta H^\circ_I = 86.93 \pm 1.45$ kcal/mole was obtained. Using $\Delta H^\circ_{298} = \Delta H^\circ_I + \Delta a\ T + \frac{\Delta b T^2}{2} + \frac{\Delta c}{T}$ gives $\Delta H^\circ_{298} = 87.06 \pm 1.45$ kcal/mole.

For the third-law calculation, free-energy functions have been estimated in 500° intervals.[13] These data were combined with pressure data to yield ΔH°_{298} values in the equation $\Delta H^\circ_{298} = -RT \ln P - T \frac{\Delta F^\circ_T - \Delta H^\circ_{298}}{T}$. Four datum points collected at pressures for which $\lambda/d < 0.5$ were rejected. The average ΔH°_{298} value for the 10 points taken with the smaller orifice diameter is 90.48 ±0.36 kcal/mole. That for the 17 points taken with the larger orifice is 90.19 ±0.22 kcal/mole. For the 27 points for which $\lambda/d > 0.5$, an average 90.29 kcal/mole is calculated. The indicated errors are the calculated standard deviations.

The small standard deviations for the third-law heats indicate fair reproducibility of measurements. Along with uncertainty in measurements, errors in the estimated free-energy functions and heat capacities must be included to obtain actual uncertainties. These functions may be in error by enough to contribute as much as 4 kcal error to the calculated heats at 298°K; however, the heat of sublimation calculated by the third-law method is probably correct to within ±2 kcal/mole.

The results of this and earlier vapor studies are shown in Fig. 1. The solid lines of the graph are the least square fit to the three sets of data with the line for this work being calculated where $\lambda/d > 0.5$. Brewer et al.[13] suggest $\Delta H^\circ_{298} = 88$ kcal/mole based on the earlier work of Ruff and LeBoucher. Blue et al.[2] in the mass spectrometer study found $\Delta H^\circ_{298} = 92.3$ kcal/mole by the third-law method using the free-energy functions as recommended by Brewer[13] and $\Delta H^\circ_{298} = 93.8$ kcal/mole by the second-law method. The third-law value found from the Langmuir study was $\Delta H^\circ_{298} = 92.4$ kcal/mole, while that by the second-law was $\Delta H^\circ_{298} = 94.4$ kcal/mole.

The same free energy functions were assumed in the work of Blue et al. and in this work. Nearly the same temperature ranges were employed in the two studies. Therefore, the differences in calculated heats of sublimation at 298°K reflect only the systematic differences in measurements and not possible errors in the free-energy functions. Apparently, a significant discrepancy exists, therefore, between the results of this study and the results of the previous studies of barium fluoride sublimation.

The third-law ΔH°_{298} value from the study of Blue et al.[14] for CaF_2 was also about 2 kcal higher than the value calculated by Schulz and Searcy[5] from a torsion effusion study. The systematic difference in the results obtained by the two techniques may indicate a systematic error in measurement of temperature or may indicate that the Langmuir data with which Blue's measurements were normalized were not equilibrium measurements. A low sublimation coefficient for barium fluoride would cause Langmuir pressures to be less than the equilibrium pressures.

The best way to identify the source of the discrepancy appears to be to conduct Langmuir free-surface sublimation experiments in our torsion-effusion apparatus. Temperature measurement errors and other systematic errors would largely cancel when pressures are measured by effusion and by free-surface sublimation in the same apparatus. If lower apparent pressures are obtained in free-surface sublimation experiments than have been obtained in effusion experiments, a low sublimation coefficient must be concluded to characterize barium and calcium fluoride sublimation.

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APPENDIX

A. Orifice Dimensions[+]

Cell	Hole Diameter (cm)		Channel length (cm)		Channel factor (cm)		Moment Arm. (cm)	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1	0.236	0.234	0.13	0.13	0.712	0.712	1.266	1.188
2	0.107	0.105	0.13	0.13	0.524	0.5193	1.200	1.163

[+] Torsion constant for all runs was 2.26 dny-cm-rad^{-1}.

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