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

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ABSTRACT

The vapor pressure of barium fluoride was measured in the temperature

range 1261° to 1548°K by the torsion-effusion method. The free-surface

sublimation pressure from the [111] faces of single crystals was measured

by the torsion-Langmuir method in the range 1315° to 1492°K. Comparison

of the torsion-effusion and torsion-Langmuir data indicates a sublimation

coefficient of 1.0 ± 0.1. Extrapolation of the data in the Langmuir

experiments yields a heat of sublimation at 298°K of 90.41 ± 3 kcal/mole

and for the Knudsen experiments yields 90.25 ± 3 kcal/mole by the third-

law method and 88.9 ± 3 kcal/mole and 88.8 ± 3 kcal/mole by the second-

law method.

INTRODUCTION

Measurements of the vapor pressure of barium fluoride have been made by Ruff and LeBoucher[1] between 1960° and 2206°K by use of a dynamic method, by Green et al.[2] by means of a Knudsen effusion study with a mass spectrometer between 1232° and 1505°K, by Hildenbrand et al.[3] by means of a torsion-effusion study between 1300° and 1550°K, and by Bautista and Margrave[4] by means of a weight loss study on single crystals between 1167° and 1250°K.

From a comparison of various effusion and free-surface evaporation studies, Bautista and Margrave[4] suggest that the evaporation coefficient for alkaline earth fluorides and chlorides are in the range 0.1 to 0.3.

However, the free-surface and effusion experiments compared were in no case performed in both the same apparatus and in the same temperature range, so that the apparent differences in measured pressures could arise from systematic experimental errors. It therefore seemed desirable to measure the vapor pressure of some alkaline earth difluoride by an effusion and by a Langmuir method in a single apparatus. Since one of us[5] had already obtained some torsion-effusion data for barium fluoride and since single crystals of barium fluoride were available, barium fluoride was chosen as the substance for study by the torsion-effusion[6,7] and torsion-Langmuir[8] methods.

EXPERIMENTAL

Barium fluoride in the form of powder of optical quality and of single crystals was obtained from Semi Elements, Incorporated.

The torsion apparatus that was used in this work is described by

Hammer and Pask.[9] The apparatus makes use of the interaction of an electric field with a small permanent magnet to balance the torque produced by effusion of vapor from orifices or surfaces which are offset from the center of support. Calibration of the apparatus was effectuated in the manner described by Hammer and Pask. For the present study, the torsion cells were made of National Carbon ZT-101 graphite in box shape. Pairs of orifices with three different areas[10] were used in the Knudsen experiments. Corrections for the finite orifice lengths[11] were made in calculations from the data. Before effusion holes were machined in the cell walls, each cell was heated with barium fluoride inside. No observable deflection was found when the cells and samples were heated to 1450°K. Therefore, it was assumed that measured deflections during the experiment were due only to effusion of vapor through the orifices.

In the Langmuir free-surface evaporation experiments, cleaved [111] faces of barium fluoride single crystals were placed behind graphite washers mounted in the verticle cell walls. Two different washer orifice areas [12] were used to prove that leakage through or around the washers and deflections of evaporating molecules from the beveled washer walls did not constitute significant sources of error. The exterior face of each washer was beveled to zero thickness at the center hole. Microscopic examination at 250X of single crystals heated at 1450°K for 45 min showed no roughening of the [111] surface near the center of the region exposed for evaporation. Toward the edges of the exposed surfaces, successive edges of [111] surfaces rose from the flat central region toward the original crystal surface. The correction for molecules

reflected or condensed near the edges of the exposed surface are demonstrated to be negligible by the fact that data obtained from surfaces whose areas differed by a factor of 4 were in excellent agreement.

The furnace heating elements were of hairpin-shaped tungsten wires connected in parallel. Electromagnetic repulsion of the torsion assembly which was noted in other torsion-effusion work,[13] was not observed because of the self-cancelling of the induced-field in the hairpin elements. Temperatures were measured by a thermocouple placed in a reference graphite cell located below the effusion cell in the furnace hot zone. To calibrate the effusion cell temperature against the reference cell temperature, a thermocouple was mounted in an effusion cell. This thermocouple was calibrated by a gold point determination when both cells were in the vapor pressure apparatus. The relative temperatures of thermocouples in the reference and effusion cells were measured at a series of power settings.

The equilibrium vapor pressure of tin was measured by the torsion-effusion method to check for any systematic errors that would affect pressure readings. The third-law heat of sublimation of tin at 298°K was determined as ΔH^o_{298} = 71.79 ± 0.27 kcal/mole. In an exhaustive study of tin by the same method, Schulz[14] found ΔH^o_{298} = 71.8 kcal/mole compared with ΔH^o_{298} = 72.2 kcal, the value suggested by Hultgren et al.[15] from earlier studies.

Prior to a run, the cell and sample were heated 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 x 10^{-5} torr. 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.

RESULTS AND DISCUSSION

The results of this study are shown in Fig. 1 and in Tables I and
II. The lines of the graph are the least squares fit to the data collected.

Molecular flow equations for low-pressure gas flow through an orifice
have been shown to apply only when the mean free path of the vapor species
is greater than some critical value that depends on the dimensions of the
effusion orifice.[16,17] Mean free path to diameter ratios were calculated
using the hard spheres approximation[18] with the molecular diameter of
barium fluoride taken as 8.14Å, the sum of ionic diameters at room
temperature, assuming a linear molecule. This value of λ/d can be used
only for relative comparison. Recent experiments[19] indicate barium
fluoride may be a bent molecule and thus would have a slightly smaller
effective molecular diameter than assumed. Knudsen pressures for which
calculated λ/d values are less than 1.0 are excluded in the final calculations
of the heats of sublimation and are not shown in Fig. 1 because systematic
deviations in calculated values, presumably arising from failure of the
molecular flow approximation, are apparent for measurements at lower λ/d's.
For orifice 1 when λ/d was less than 1.0, ΔH^o_{298} values of 1.54 to 1.28
kcal/mole below the average were found. Schulz and Searcy[13] also found
substantial deviation in ΔH^o_{298} values when λ/d became less than a critical
value near unity.

Least-square calculations from Knudsen data where $\lambda/d > 1.0$ yield

for the vapor pressure in atmospheres $\log P = -\left(\frac{79.73 \pm 0.77}{4.576}\right) \times \frac{10^3}{T} +$

7.15 ± 0.12 between $1261°$ and $1548°K$ and $\log P = -\left(\frac{80.08 \pm 1.2}{4.576}\right) \times \frac{10^3}{T} +$

7.18 ± 0.28 between $1315°$ and $1492°K$ for the Langmuir experiment. The

errors are the standard deviations from the least-squares fits.

The heats of sublimation of barium fluoride at $298°K$ for the

Knudsen and Langmuir data were calculated by both the second-law and

third-law methods. In all calculations, BaF_2 was considered to be the

major vapor species[2] because thermodynamic calculations indicate that

the pressures produced by the reactions $BaF_2(s) + C(s) = BaF(g) + CF(g)$,

$BaF_2(s) + C(s) = Ba(g) + CF_2(g)$ and $BaF_2(c) + 1/2C(s) = BaF(g) + 1/2CF_2(g)$,

would be several orders of magnitude below the observed pressures.

The same heat capacity equations and free energy functions for solid

barium fluoride[20] and the same estimated heat capacity and free energy

functions for barium fluoride gas[21] were used in calculating heats of

sublimation as were used by Green et al.[2] and by Bautista and Margrave.[4]

The free energy functions used are expected to be as reliable as can

presently be estimated[21] whether or not the $BaF_2(g)$ molecule is linear

or bent as suggested by recent electric dipole studies.[19] The second-law

treatment yielded $\Delta H^{\circ}_{298} = 88.78 \pm 1.26$ kcal/mole from the Knudsen experiments

and $\Delta H^{\circ}_{298} = 88.94 \pm 1.75$ kcal/mole from the Langmuir experiments. The

third-law calculations for the 46 Knudsen measurements for which $\lambda/d > 1.0$

yielded $\Delta H^{\circ}_{298} = 90.25 \pm 0.28$ kcal/mole and for the 25 Langmuir measurements

yielded $\Delta H^{\circ}_{298} = 90.41 \pm 0.35$. The indicated errors are the standard

deviations. The free energy functions could be in error by enough to

contribute a 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 ± 3 kcal/mole. Assuming a $+5°$ error at the high end of

measurements and a $-5°$ error at the lower end, (correspondingly $\pm 10\%$

errors in pressures) yields an estimated maximum error of 2.8 kcal for

the second law calculation.

Brewer et al.[21] concluded from the early work of Ruff and LeBoucher[1]

that the heat of sublimation of barium fluoride is about 88 kcal/mole at

298°K. Green et al.[2] in the mass spectrometer study found $\Delta H°_{298} = 92.3$

kcal/mole by the third-law method and $\Delta H°_{298} = 93.8$ kcal/mole by the

second-law method. Torsion-effusion studies of Hildenbrand et al.[3]

yield $\Delta H°_{298} = 88.6$ kcal when recalculated with the same free energy

functions used by the other investigators. The Langmuir measurements of

Bautista and Margrave[4] yield $\Delta H°_{298} = 92.3$ kcal/mole from third law analysis

and $\Delta H°_{298} = 94.7$ kcal/mole by second law analysis.

Hildenbrand and coworkers[3] believe their experimental results indicate

that barium fluoride is bent. We will not comment further on this point

because the work of Hildenbrand et al. is not yet published except in

company reports. The second and third law measurements of the present

work agree well when Brewer's[21] free energy functions are used.

Since the same free energy functions were used by Green et al.,[2]

by Bautista and Margrave[4] and by us and since the measurements were

made in approximately the same temperature ranges, the differences in

calculated heats of sublimation at 298°K reflect the systematic differences

of approximately a factor of 2 in measured pressures and not possible

errors in the free-energy functions. Mass spectrometer pressure measure-

ments are usually expected to be uncertain by a factor of two or more. It was primarily comparison of the Langmuir data with effusion measurements of other investigators that led Bautista and Margrave[4] to hypothesis that evaporation coefficients for alkaline earth halides generally lie in the range 0.1 to 0.3. Recently, however, Loehman, Kent and Margrave[22] have measured Knudsen data of strontium chloride above its melting point and Langmuir data below. The Langmuir experiments were proformed on single crystals suspended in the furnace. Extrapolation of their Knudsen data into the range below the melting point clearly indicates an evaporation coefficient of 0.3 for the solid. For barium fluoride, comparison of Bautista's results to our effusion results leads to the conclusion that the value of α is about 0.5.

Comparison of our own free surface and effusion data, however, yields $\alpha = 1.0 \pm 0.1$. The <u>relative</u> error in our measurements of free surface and effusion data should probably not exceed 10% because most sources of systematic error are common to the free surface and effusion measurements. The most probable source of serious error in determination of α is a discrepancy between measured temperature and true temperature of the evaporating surface of a Langmuir sample. In this research the Langmuir specimens were mounted in the same position as the orifices of the effusion cells in a chamber of demonstrated uniform temperature. If the true value of α were 0.5 our free surface temperatures would have to be approximately 35° higher than the temperature inside an effusion cell placed in the same positions in order to account for the results presented in this paper. An actual temperature difference of more than

five degrees is very unlikely.

The 111 surfaces of the barium fluoride surfaces remained smooth when examined at 240 magnifications; surface roughening did not, therefore, significantly increase the effective rate of evaporation. The evaporation coefficient for this face of a barium fluoride crystal is unity within a small probable experimental error, and the evaporation coefficients for other alkaline earth fluorides are probably also unity.

ACKNOWLEDGMENTS

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    Orifice Pair 2, diameter 2.36 mm, length 1.30 mm

    diameter 2.34 mm, length 1.30 mm

    Orifice Pair 3, diameter 0.46 mm, length 0.75 mm

    diameter 0.46 mm, length 0.77 mm.

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    diameter 1.98 mm

    Orifice Pair 5, diameter 0.99 mm

    diameter 0.98 mm.

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Table I. Torsion-effusion sublimation pressures for barium fluoride.[†]

T, °K	P, atm	$-\left(\dfrac{\Delta F^o_T - \Delta H^o_{298}}{T}\right)$ cal/deg	ΔH^o_{298} kcal/mole
1491	3.32×10^{-5}	39.77	89.81
1459	1.69×10^{-5}	39.96	90.17
1440	1.03×10^{-5}	40.07	90.57
1414	5.83×10^{-6}	40.22	90.74
1388	3.56×10^{-6}	40.35	90.61
1548	1.24×10^{-4}	39.42	88.71*
1520	6.90×10^{-5}	39.57	89.09*
1358	1.59×10^{-6}	40.46	90.99
1378	2.56×10^{-6}	40.39	90.92
1395	3.95×10^{-6}	40.32	90.70
1425	8.77×10^{-6}	40.10	90.21
1358	2.18×10^{-6}	40.47	90.55
1448	1.44×10^{-5}	40.03	90.03
1526	7.55×10^{-5}	39.57	89.17*
1401	5.27×10^{-6}	40.28	90.27
1305	6.10×10^{-7}	40.69	90.22
1430	9.90×10^{-4}	40.13	90.13
1388	3.80×10^{-6}	40.37	90.46
1402	5.22×10^{-6}	40.27	90.33
1293	4.68×10^{-7}	40.74	90.13
1308	6.76×10^{-7}	40.67	90.13
1318	8.70×10^{-7}	40.64	90.12
1375	3.08×10^{-6}	40.41	90.25
1359	2.13×10^{-6}	40.48	90.28
1277	3.47×10^{-7}	40.82	89.87
1261	2.52×10^{-7}	40.89	89.64
1375	3.10×10^{-6}	40.41	90.22
1384	4.20×10^{-6}	40.37	89.92
1370	2.53×10^{-6}	40.43	90.48
1350	1.73×10^{-6}	40.52	90.29
1336	1.19×10^{-6}	40.58	90.43
1455	1.44×10^{-5}	39.98	90.40
1390	4.04×10^{-6}	40.33	90.36
1431	9.22×10^{-6}	40.12	90.39
1486	2.70×10^{-5}	39.80	90.21
1486	2.95×10^{-5}	39.80	90.05
1506	3.73×10^{-5}	39.69	90.29

Table I. Continued

T, °K	P, atm	$-\left(\dfrac{\Delta F^{\circ}_T - \Delta H^{\circ}_{298}}{T}\right)$ cal/deg	ΔH°_{298} kcal/mole
1535	5.86×10^{-5}	39.53	90.41
1394	4.76×10^{-6}	40.32	90.24
1413	7.52×10^{-6}	40.22	89.96
1440	1.13×10^{-5}	40.07	90.30
1464	1.99×10^{-5}	39.93	89.95
1473	2.34×10^{-5}	39.88	89.95
1548	7.11×10^{-5}	39.45	90.45
1360	2.02×10^{-6}	40.48	89.49
1523	4.93×10^{-5}	39.58	90.30
1395	4.51×10^{-6}	40.32	90.37
1501	3.66×10^{-5}	39.72	90.09
1529	5.29×10^{-5}	39.55	90.39

ave = 90.25 ± 0.28

*Indicates where λ/d was calculated to be less than 1.0

†First 14 points taken with orifice set 1
Middle 18 points with orifice set 2
Last 18 points with orifice set 3

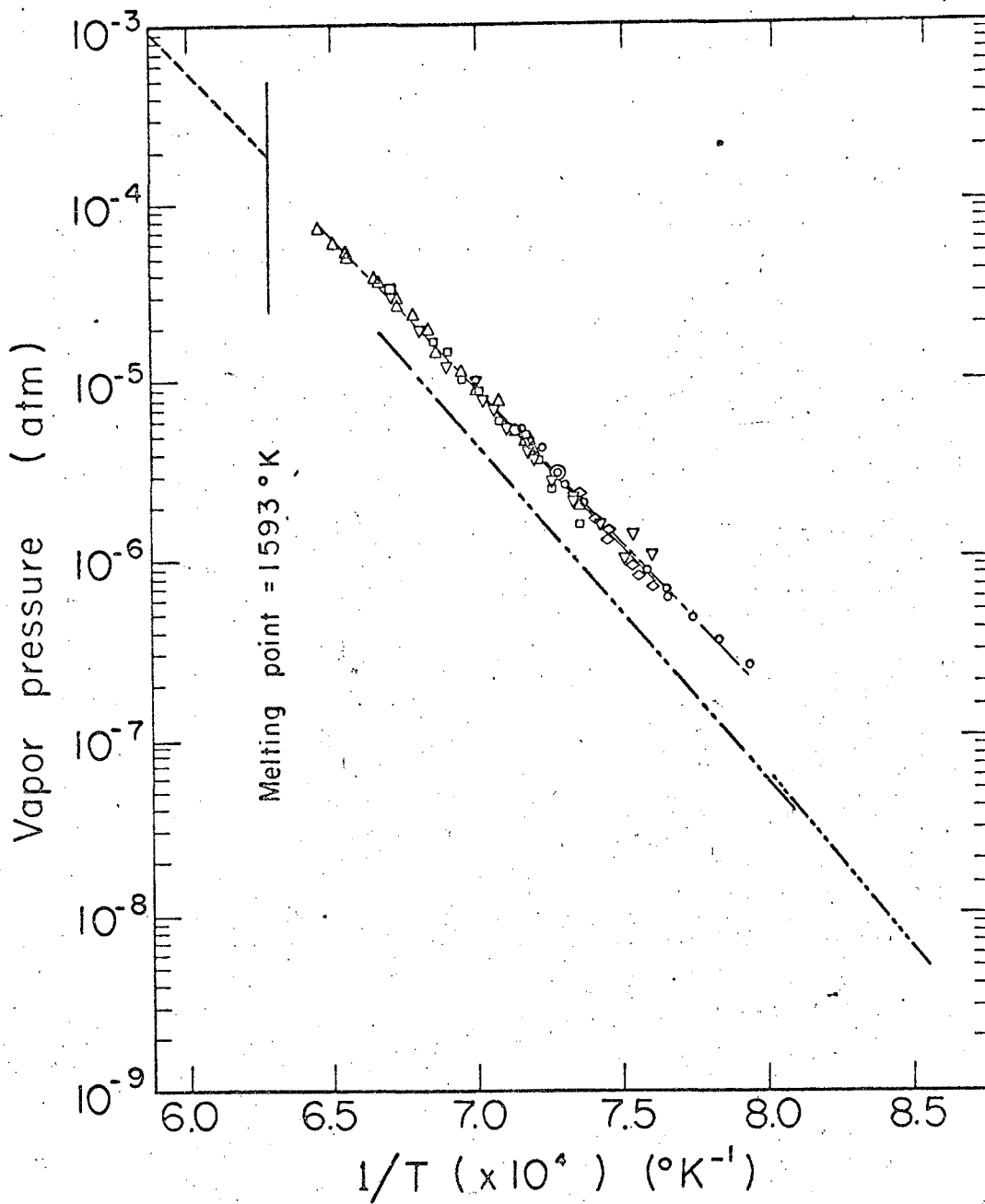Table II. Torsion-Langmuir Sublimation Pressure for Barium Fluoride[†]

T, °K	P, atm	$-(\dfrac{\Delta F^{\circ}_{T} - \Delta H^{\circ}_{298}}{T})$ cal/deg	ΔH°_{298} kcal/mole
1445	1.19×10^{-5}	40.05	90.42
1470	1.91×10^{-5}	39.90	90.70
1492	2.86×10^{-5}	39.75	90.33
1318	1.04×10^{-6}	40.63	89.63
1394	3.90×10^{-6}	40.31	90.69
1425	7.66×10^{-6}	40.16	90.59
1395	4.40×10^{-6}	40.31	90.42
1390	3.56×10^{-6}	40.34	90.73
1331	1.37×10^{-6}	40.59	89.73
1347	1.58×10^{-6}	40.53	90.34
1365	2.23×10^{-6}	40.45	90.51
1417	6.51×10^{-6}	40.20	90.52
1365	2.14×10^{-6}	40.45	90.63
1408	5.41×10^{-6}	40.24	90.60
1377	2.70×10^{-6}	40.40	90.71
1430	9.68×10^{-6}	40.12	90.18
1402	5.27×10^{-6}	40.28	90.33
1331	9.63×10^{-7}	40.59	90.68
1328	9.19×10^{-7}	40.60	90.61
1315	6.84×10^{-7}	40.65	90.55
1345	1.23×10^{-6}	40.53	90.88
1323	7.85×10^{-7}	40.62	90.70
1340	1.44×10^{-6}	40.55	90.16
1361	2.25×10^{-6}	40.48	90.27
1350	1.70×10^{-6}	40.52	89.34

ave = 90.41 ± 0.35

[†]First 18 points with orifice set 4
Last 7 points with orifice set 5

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Figure Caption

Figure 1. Vapor Pressure of Barium Fluoride

_____ _ _____   Knudsen experiment (this work) $\lambda/d > 1.0$

□ orifice 1, ○ orifice 2, △ orifice 3;

_____   Langmuir experiment (this work)

▽ orifice 4, ◇ orifice 5;

_ _ _ _ _   Buff and LeBouche (extrapolated);

__ _ _ __   Green et al.;

__ _ _ __   Bautista and Margrave.

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