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VAPOR PRESSURE OF THORIUM TETRAFLUORIDE

BY

A. J. DARNELL
F. J. KENESHEA, JR.

ATOMICS INTERNATIONAL

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ABSTRACT

The vapor pressures of solid and liquid ThF_4 have been determined. For the solid phase, the Knudsen effusion method was used over the temperature range of 1055° to 1297° K; for the liquid, the quasi-static method of Rodebush and Dixon was used between 1437° and 1595° K. The vapor pressure equation for the solid is $\log P_{(atm)} = -16{,}860/T + 9.105$; and for the liquid, $\log P_{(atm)} = -15{,}270/T + 7.940$. The heat of vaporization at the extrapolated boiling point (1953° K) is 61.6 kcal per mole, using an estimate of -19 cal per deg per mole for ΔCp. Both the vapor pressure results and a mass spectrometric examination of the vapor indicate that thorium tetrafluoride vaporizes as the monomer.

I. INTRODUCTION

No experimental determination of the vapor pressure of thorium tetrafluoride is reported in the literature, although an estimate has been made by Brewer[1].

In the present work, the Knudsen[2] effusion method was used to determine the vapor pressure of the solid, and the quasi-static method of Rodebush and Dixon[3] was used to determine the vapor pressure of the liquid. These two methods were used to extend the measurements over as wide a range as practicable in the solid and liquid states, in order to obtain values for the heats of sublimation and vaporization of ThF_4.

A mass spectrographic analysis was made to determine the gaseous species vaporizing from ThF_4.

II. EXPERIMENTAL

The ThF_4 used in these experiments was obtained from the A. D. Mackay Company. An X-ray diffraction pattern of the sample showed only ThF_4 lines. Chemical analysis of the salt gave a value of 75.3 ± 0.2 weight per cent thorium, (theoretical 75.33). Weight loss experiments also showed less than 0.2 per cent volatile impurities. The melting point was determined by thermal analysis to be 1110 ± 2° C, which is to be compared with a literature value[4] of 1111° C.

Temperature measurements were made with Pt:Pt 10 per cent Rh thermocouples calibrated at the melting point of recrystallized NaCl. The temperature of the ThF_4 was held constant during vapor pressure determinations by means of a Leeds and Northrup potentiometric type controller-recorder.

Nickel cells were used to contain the ThF_4 in the effusion and quasi-static experiments. A corrosion test with molten ThF_4 showed less than 0.005 per cent nickel contamination from the crucible.

A. EFFUSION METHOD

The effusion cell was fitted with a screw cap and interchangeable thin lids with various orifice diameters. The inside dimensions of the cell were 1/2 in. by 1 in. The cell was heated by a Marshall tube furnace adjusted to obtain a uniform temperature region (± 2° C) extending 1 in. beyond the ends of the cell. The error in the effusion time was held below 1 per cent by use of brief heat-up and cool-off intervals in the cell.

The quantity of material effused was determined from the weight loss of the cell during an experiment. In one run, the effusate was condensed on a cylindrical tantalum collector; within experimental accuracy, the amount collected was equal to the weight loss of the cell. The effusate was analyzed by X-ray diffraction and chemical analysis, and was found to be ThF_4.

B. QUASI-STATIC METHOD

The quasi-static method, in essence, yields the pressure at which the salt boils for a given temperature. This method is described by Rodebush and Dixon[3], and was used by Fiock and Rodebush[5] to measure the vapor pressure of some of the alkali halides. The nickel cell employed here is similar to the quartz cell used by Fiock and Rodebush[5]. Two nickel tubes were welded into the top of the cell to hold the reflux capillaries. The upper end of one of these tubes was connected to a vacuum system through a stopcock. The upper end of the other tube was connected to an absolute manometer filled with H_2SO_4. A differential manometer containing Amoil-5 was connected between the two tubes. Two thermocouple wells were placed in the cell; one immersed in the liquid salt, and the other in the vapor immediately above the liquid. The temperature of the liquid and vapor always agreed within 3° C, and values obtained for the liquid were used in the calculations.

To prevent its collapse, the nickel cell was enclosed in an evacuated porcelain tube. This precaution was necessary because, at the temperatures used, nickel lacks sufficient mechanical strength to withstand an external pressure of one atmosphere. The cell and protection tube were vertically mounted in a Hoskins Model FHS-304 tube furnace.

Vapor pressure measurements were made by starting with an inert gas pressure greater than the vapor pressure of the salt, then reducing the pressure by small increments until the first "permanent difference" was obtained in the differential manometer. Under this condition, the vapor pressure of the salt was equal to the pressure of the inert gas at the absolute manometer.

C. MASS SPECTROMETRIC INVESTIGATION OF VAPOR

The vapor effusing from an inductively heated Knudsen cell containing ThF_4 was examined with a Bendix time-of-flight mass spectrometer, using 75-v electrons. The nickel cell containing the salt was mounted in a manifold so that the vapor would pass into the ionizing region of the mass spectrometer.

This system was connected to a conventional vacuum pump which provided a background pressure of less than 5×10^{-5} mm Hg. The temperature of the salt was determined by "sighting" into the cell orifice with an optical pyrometer. Inspection of the positive ion fragments formed from ThF_4 vapor was made over the temperature range of 900° to 1200° C.

III. RESULTS AND DISCUSSION

The experimental data obtained from the effusion experiments are presented in Table I. The pressure was calculated from the Knudsen effusion equation,

$$P_{(atm)} = \frac{0.02255\,g}{K\,a\,t}\sqrt{\frac{T}{M}} \qquad \ldots(1)$$

where g = grams of material effused,

K = Clausing[6, 7] factor,

a = area of orifice in cm^2,

t = time interval in sec,

T = temperature, °K,

and M = molecular weight of vapor.

Three orifices were used with area ratios of approximately 1 to 4 to 8. The pressures obtained were independent of hole size within the experimental accuracy of the determination, indicating that the vapor was at equilibrium with the solid. Effusion experiments were performed up to pressures of 0.1 mm Hg; above this pressure, the viscous flow contribution complicates the treatment of the effusion data.

The data from the quasi-static experiments are given in Table II. This method has been used by Fiock and Rodebush[5] in the pressure range of 6 to 55 mm Hg. To check the applicability of the method below 6 mm, measurements were made on NaCl; the results down to 1.5 mm Hg agreed with those in the literature[5, 8]. Below this pressure, the quasi-static method gave low and erratic results. These were probably caused by effusion of inert gas through the vapor tubes at such low pressures, thus making it difficult to detect a "permanent difference" in pressure between the legs of the cell. The upper limit of the quasi-static pressure measurements was set by loss of mechanical strength of the nickel cell at high temperatures.

TABLE I

VAPOR PRESSURE OF SOLID THORIUM TETRAFLUORIDE BY THE KNUDSEN EFFUSION METHOD

Temp (° K)	Wt loss (gms)	Time (sec)	Orifice* (cm^2)	Pressure (atm)
1055	0.0150	3.32×10^5	c	1.21×10^{-7}
1066	0.0259	3.38×10^5	c	2.06×10^{-7}
1077	0.0295	2.42×10^4	c	3.31×10^{-7}
1113	0.0066	2.35×10^5	a	8.55×10^{-7}
1113	0.0724	2.38×10^5	c	8.36×10^{-7}
1166	0.0212	1.52×10^5	a	4.33×10^{-6}
1184	0.0256	1.20×10^4	c	6.08×10^{-6}
1186	0.1651	6.35×10^4	c	7.41×10^{-6}
1212	0.0386	1.30×10^5	a	1.39×10^{-5}
1214	0.0354	6.02×10^4	a	1.87×10^{-5}
1218	0.0480	6.22×10^4	a	2.47×10^{-5}
1225	0.0515	1.35×10^4	b	2.38×10^{-5}
1277	0.0393	1.70×10^4	a	7.54×10^{-5}
1297	0.0552	1.47×10^4	a	1.23×10^{-4}

*Orifice areas (cm^2) and Clausing correction factors (K) were, respectively: a, 0.00196, 0.65; b, 0.00815, 0.82; c, 0.0164, 0.86.

TABLE II

VAPOR PRESSURE OF LIQUID THORIUM TETRAFLUORIDE BY THE QUASI-STATIC METHOD

Temp (°K)	Pressure (atm)
1437	2.03×10^{-3}
1459	3.15×10^{-3}
1466	3.07×10^{-3}
1466	2.64×10^{-3}
1469	3.91×10^{-3}
1470	3.96×10^{-3}
1477	4.09×10^{-3}
1484	5.03×10^{-3}
1499	5.88×10^{-3}
1501	6.07×10^{-3}
1529	9.34×10^{-3}
1532	8.77×10^{-3}
1535	9.71×10^{-3}
1555	1.33×10^{-2}
1575	1.72×10^{-2}
1575	1.71×10^{-2}
1595	2.44×10^{-2}

Results from the two methods are plotted in the figure. Equations for the vapor pressure of the solid and of the liquid were obtained by least squares treatments of the log P vs 1/T data. The equations are:

$$\text{sublimation, } \log P_{(atm)} = \frac{-(16{,}860 \pm 190)}{T°K} + (9.105 \pm 0.160), (1055\text{-}1297° K) \ldots (2)$$

$$\text{vaporization, } \log P_{(atm)} = \frac{-(15{,}270 \pm 310)}{T°K} + (7.940 \pm 0.206), (1437\text{-}1595° K) \ldots (3)$$

Vapor pressure measurements were not carried out at the melting point because neither method is applicable in this pressure range. Comparison of the results was made by extrapolating equations (2) and (3) to the melting point (1383° K). By so doing, vapor pressures of 8.2 x 10-4 and 7.9 x 10^{-4} atmospheres, respectively, were obtained.

The heats of sublimation and vaporization at the midtemperatures in each set of experimental data are:

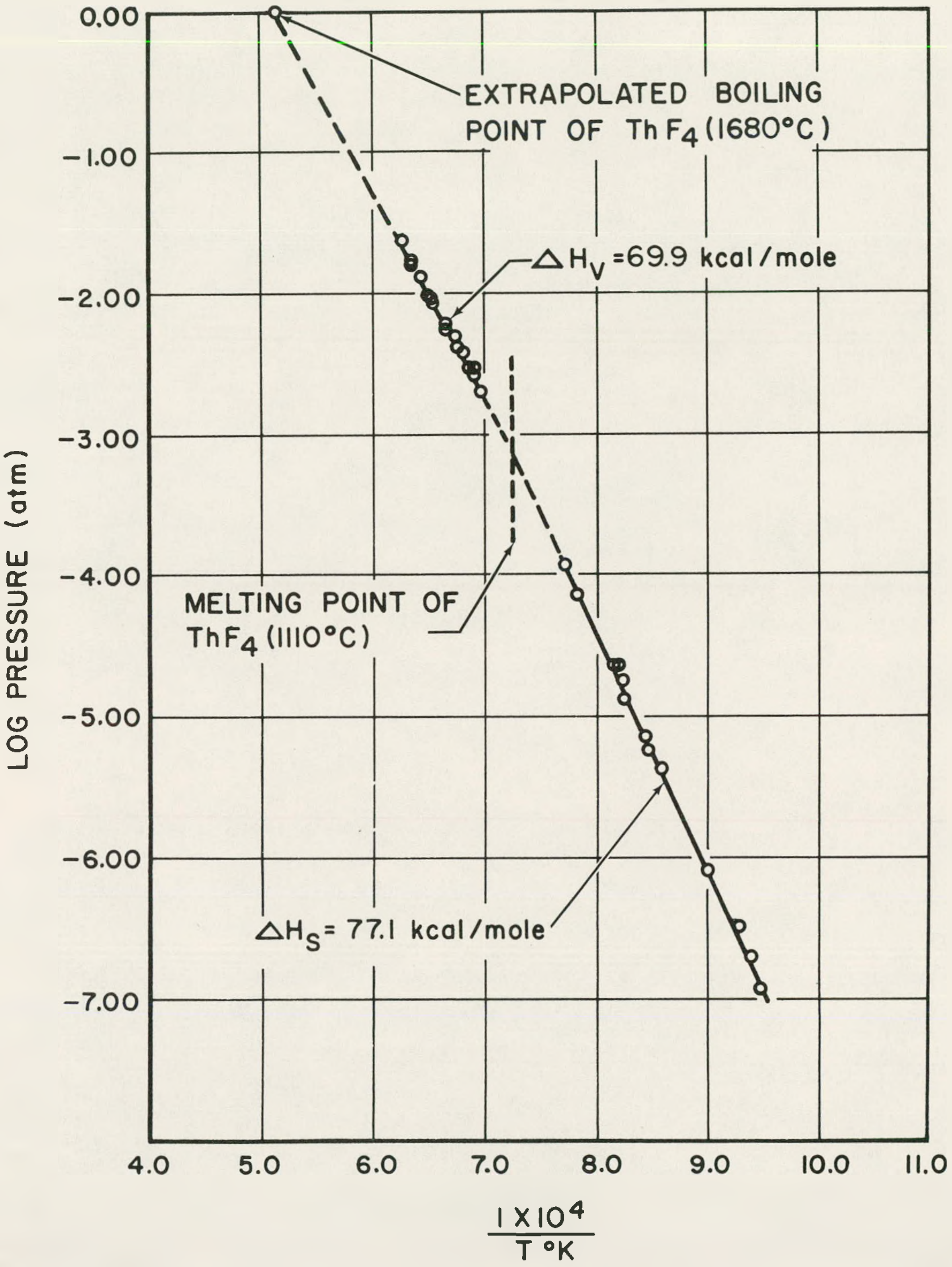
$$\Delta H_{1176}\text{(subl)} = 77.1 \pm 0.9 \text{ kcal per mole} \qquad \ldots (4)$$

$$\Delta H_{1516}\text{(vap)} = 69.9 \pm 1.5 \text{ kcal per mole.} \qquad \ldots (5)$$

The Δ Cp of vaporization (-19 cal/deg/mole) estimated for the other tetrahalides of thorium by L. Brewer, and reported in N.B.S. Circular 500[9], was used in the free energy of vaporization equation,

$$\Delta F°_T = \Delta H_o - \Delta C_p T \ln T + IT. \qquad \ldots (6)$$

The constants ΔH_o and I are evaluated from (3) as 98,660 and -194.50, respectively. Equation (6) gives a normal boiling point of 1953° K for ThF_4. Application of this ΔC_p correction to (5) yields; ΔH_{1953}(vap) = 61.6 kcal/mole, ΔS_{1953}(vap) = 31.5 cal/deg/mole.



Vapor Pressure of Thorium Tetrafluoride

By comparing the vapor pressure data from the two methods, certain conclusions may be drawn regarding the vapor species of ThF_4. The quasi-static method gives the total pressure above the salt. Pressures resulting from the effusion method were calculated by assuming that $ThF_4(g)$ was the monomer. The agreement of the two sets of pressure data secured by extrapolating to the melting point, constitutes good evidence that ThF_4 vaporizes as the monomer. This conclusion is further substantiated by mass spectrographic studies made on ThF_4 effusing from a Knudsen cell. The predominant peak was due to mass 289; smaller peaks representing masses of 270, 251, and 232 were also observed. These masses are attributed to ionization of $ThF_{4(g)}$ to ThF_3^+, ThF_2^+, ThF^+, and Th^+. Corresponding peaks for the dimer of ThF_4 were not observed over the temperature range of these measurements.

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