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THE FREE ENERGY, HEAT, AND ENTROPY OF FORMATION OF THORIUM OXYFLUORIDE

By
A. J. DARNELL

ATOMICS INTERNATIONAL

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ABSTRACT

Thorium oxyfluoride, $ThOF_2$, decomposes at elevated temperatures to $ThO_2(s)$ and $ThF_4(g)$. The equilibrium pressure of ThF_4 from the decomposition of $ThOF_2$ was measured in a Knudsen effusion cell from 1109 to 1286°K. The pressure of ThF_4 from the decomposition reaction is

$$Log\, P_{(atm)} = - \frac{17{,}630 \pm 370}{T(°K)} + 9.363 \pm 0.302$$

The free energy, enthalpy, and entropy of formation of $ThOF_2(s)$ at 298°K are -371.2 kcal/mole, -389.6 kcal/mole, and -62.0 cal/deg-mole, respectively.

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I. INTRODUCTION

The preparation of thorium oxyfluoride from partial hydrolysis of thorium tetrafluoride in moist air at elevated temperatures has been reported by Chauvenet[1] and D'Eye.[2] However, no thermochemical data are reported in the literature for thorium oxyfluoride. Chauvenet[1] obtained the heats of formation of thorium oxychloride, oxybromide, and oxyiodide from a study of the reactions of the corresponding tetrahalides with water. However, he was unable to obtain the heat of formation of thorium oxyfluoride by this method because of the inertness of thorium tetrafluoride to water.

A method similar to that employed for uranous oxybromide[3] and uranous oxychloride[4] has been used in this work to determine the thermodynamic stability of thorium oxyfluoride with respect to its decomposition products thorium dioxide and thorium tetrafluoride. Data derived from the results of this decomposition reaction and thermochemical data for thorium dioxide[5] and thorium tetrafluoride[6,7] were used to calculate the free energy, enthalpy, and entropy of formation of thorium oxyfluoride.

II. EXPERIMENTAL

A. MATERIALS

Thorium oxyfluoride was prepared by a method similar to that used by D'Eye.[2] The starting materials ThO_2 and ThF_4 were of the same purity as described in a previous paper.[7] Thoria and thorium tetrafluoride of small particle size were thoroughly mixed, then compressed into pellets with a hydraulic press at a pressure of two tons per square inch. These pellets were then heated at 900°C in an atmosphere of purified argon for 16 hours. This procedure yielded $ThOF_2$ which gave X-ray diffraction patterns which agreed with the diffraction data for $ThOF_2$ reported by D'Eye.[2]

B. APPARATUS AND PROCEDURE

The pressure of ThF_4 from the decomposition of $ThOF_2$ was measured by the Knudsen effusion method. The rate of effusion of gaseous ThF_4 from the reaction cell was determined from the weight loss of the cell during a known time interval. The pressure of ThF_4 was calculated from the Knudsen effusion equation:

$$P_{(atm)} = \frac{0.02255\, g}{°K\, at} \sqrt{\frac{T}{M}} \quad . \qquad \ldots(1)$$

where,

g = weight loss of cell (gm)

K = Clausing factor

a = area of orifice (cm^2)

t = time interval (sec)

T = temperature (°K)

M = molecular weight of vapor (previous work[6] indicates that ThF_4(g) is monomeric).

The apparatus which was previously used[6] to measure the vapor pressure of solid ThF_4 was also used in this work.

III. RESULTS AND DISCUSSION

Thorium oxyfluoride was found to decompose at elevated temperatures in the following manner:

$$2ThOF_2(s) \rightleftharpoons ThO_2(s) + ThF_4(g) \quad . \qquad \ldots(2)$$

Evidence for this is based on chemical and X-ray analyses of condensed samples of the effusing vapor and of the residue in the cell. Further, pure $ThOF_2$ when decomposed completely, yielded equimolar amounts of ThO_2 and ThF_4.

Thorium tetrafluoride pressure measurements were made over a wide range of compositions of ThF_4 and ThO_2. Figure 1 shows the pressure of ThF_4 at 980°C from a sample which initially contained 20 mole % ThO_2.* The results of the effusion experiments at 20 and 34 mole % ThO_2 yield ThF_4 pressures which are in good agreement with[6] those of pure ThF_4 at this temperature.

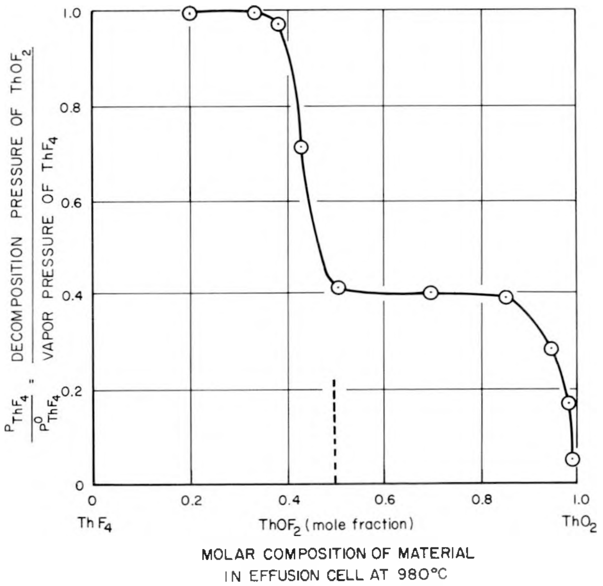

Figure 1. Pressure of ThF_4 above ThO_2-ThF_4 System Compared to Pure ThF_4 i.e., P/P° at 980°C

The pressure-composition curve exhibits a plateau which starts at about 50 mole % ThO_2 and extends to about 85 mole % ThO_2. The break in the pressure

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*Compositions are defined here in terms of the original materials, ThO_2 and ThF_4.

curve occurrs at 50 mole % ThO_2 and indicates that ThO_2 and ThF_4 react to give $ThOF_2$. In the composition range 50 to 85 mole % ThO_2, inwhich there are two solid phases, the partial pressure of ThF_4 was constant. Similar experiments at other temperatures also indicated that the pressure of ThF_4 was constant in this composition range. The pressure of ThF_4 above the system changed rapidly with a change in composition in the composition ranges 35 to 50 mole % ThO_2 and 85 to 99 mole % ThO_2. The pressures were probably not measured under equilibrium conditions since diffusion may have been the rate determining factor.

Equilibrium pressures of ThF_4 from the thermal decomposition of $ThOF_2$ were measured over the temperature range 1109 to 1286°K. The ThF_4 pressures were calculated from the effusion rate by use of Equation 1. Only those data in which less than 50% of the initial amount of $ThOF_2$ had been decomposed were used in order to remain well within the composition range of the pressure plateau of Figure 1. Orifices of four different sizes were used in carrying out the effusion experiments. The pressure calculated for the reaction cell remains constant, even though the orifice area is changed by a factor of 9, thus indicating that equilibrium exists between the vapor and the condensed phases. Calculations with the pressure-temperature data in Table I to determine slope by the method of least squares gives:

$$Log\ P_{ThF_4(atm)} = -\frac{17{,}630 \pm 370}{T(°K)} + 9.363 \pm 0.302 \quad (1109\text{–}1286°K) \quad . \qquad \ldots(3)$$

If it is assumed that the activities of the solid phases are unity and that ThF_4 behaves as an ideal gas, then the change in free energy for Reaction 2 is

$$\Delta F° = -4.576T\ log\ P_{ThF_4} \quad . \qquad \ldots(4)$$

TABLE I

EQUILIBRIUM PRESSURE OF ThF_4 FOR THE REACTION: $2\ ThOF_2(s) \rightleftharpoons ThO_2(s) + ThF_4(g)$

Temperature (°K)	Time Interval (sec)	Effused ThF_4 (gms)	Orifice*	P_{ThF_4} (atm)
1109	2.25×10^5	0.0268	c	3.12×10^{-7}
1109	2.29×10^5	0.0271	c	3.10×10^{-7}
1127	7.06×10^4	0.0140	c	5.25×10^{-7}
1128	5.85×10^4	0.0119	c	5.38×10^{-7}
1151	2.17×10^5	1.0294	b	1.20×10^{-6}
1156	5.97×10^4	0.0281	c	1.26×10^{-6}
1188	6.55×10^4	0.0748	c	3.09×10^{-6}
1193	5.76×10^4	0.0150	a	3.11×10^{-6}
1194	6.01×10^4	0.0163	a	3.23×10^{-6}
1212	3.36×10^5	0.1943	a	6.95×10^{-6}
1224	6.00×10^4	0.0509	a	1.03×10^{-5}
1232	1.74×10^4	0.0179	a	1.25×10^{-5}
1244	5.65×10^4	0.0286	d	1.77×10^{-5}
1269	7.38×10^4	0.1841	a	3.07×10^{-5}
1283	1.56×10^4	0.0184	d	4.17×10^{-5}
1286	6.60×10^4	0.2347	b	3.33×10^{-5}
1286	5.61×10^4	0.2365	a	5.23×10^{-5}

* The area and Clausing factor respectively for each of the orifices are as follows:

a) 0.00490 cm^2, 0.757
c) 0.0177 cm^2, 0.923
b) 0.00633 cm^2, 0.780
d) 0.00196 cm^2, 0.664

The vapor pressure equation for the sublimation[6] of ThF_4 i.e.,

$$ThF_4(s) = ThF_4(g) \quad , \qquad \ldots(5)$$

is

$$Log\, P^\circ_{atm}(ThF_4) = -\frac{16{,}860 \pm 190}{T(^\circ K)} + 9.105 \pm 0.160 \quad (1055\text{–}1297^\circ K) \quad . \qquad \ldots(6)$$

The free energy of sublimation is

$$\Delta F^\circ = -4.576T \log P^\circ_{ThF_4} \quad : \qquad \ldots(7)$$

Subtraction of Equation 5 from 2 gives

$$2ThOF_2(s) = ThO_2(s) + ThF_4(s) \quad . \qquad \ldots(8)$$

The free energy for Reaction 8 is then

$$\Delta F^\circ = -4.576T \log \frac{P^\circ ThF_4}{P_{ThF_4}} \qquad \ldots(9)$$

Substitution of Equations 3 and 6 into 9 gives

$$\Delta F^\circ = 3{,}524 - 1.181\, T \quad . \qquad \ldots(10)$$

No heat capacity data are available for $ThOF_2$. The ΔCp for Reaction 8 was taken to be zero, since only solid phases are involved. This assumption would also appear reasonable by comparison with the analogous case of $UOCl_2$ where heat capacity data of $UO_2(s)$, $UCl_4(s)$ and $UOCl_2(s)$ (Refrences 8, 9, and 10 respectively) show that $\Delta Cp \sim 0$.

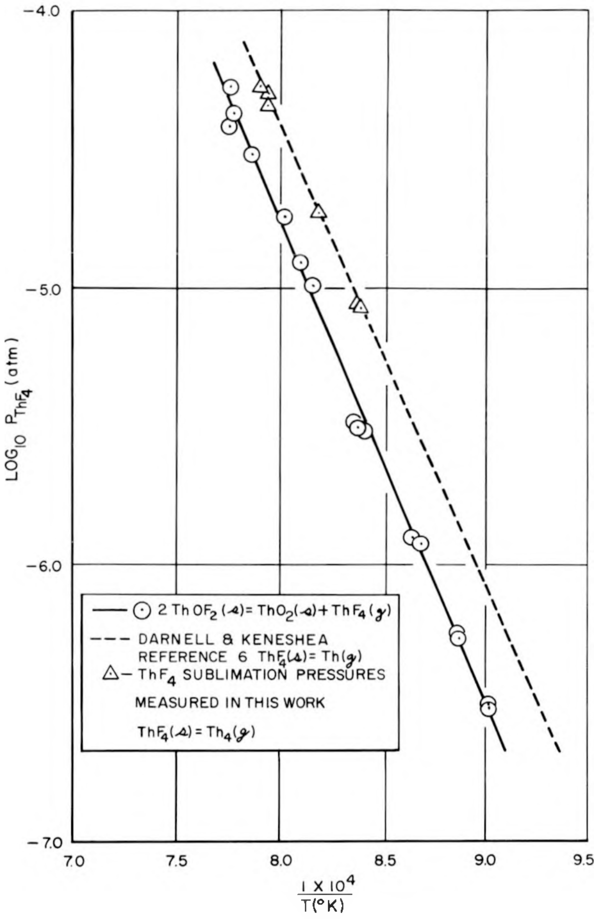

Figure 2. Pressure of ThF_4 from the Decomposition of $ThOF_2$(s) and Vapor Pressure of ThF_4 vs 1/T

TABLE II

THERMODYNAMIC DATA

Source	ΔH°_{298}(f) $\left(\frac{kcal}{mole}\right)$	ΔF°_{298}(f) $\left(\frac{kcal}{mole}\right)$	ΔS°_{298}(f) $\left(\frac{cal}{deg\text{-}mole}\right)$
Reference 5, ThO_2(s)	-293.2	-279.2	-47.0
Reference 7, ThF_4(s)	-482.4	-459.9	-75.8
<u>Reaction</u>			
$2ThOF_2(s) = ThO_2(s) + ThF_4(s)$	3.5	3.2	1.2
$ThOF_2$(s)	-389.6	-371.2	-62.0

The thermochemical data obtained for Reaction 8 at 298°K are given in Table II. These data are combined with thermochemical data for ThO_2(s) and ThF_4(s) (References 5 and 7 respectively) to obtain the enthalpy, free energy, and entropy of formation of $ThOF_2$(s), which are also given in Table II.

Figure 2 shows the pressure of ThF_4 from the decomposition of $ThOF_2$ and the vapor pressure[6] of ThF_4 vs 1/T. The ratio of these pressures P/P°, at a given temperature, is approximately 0.4 thus indicating that $ThOF_2$ is not very stable with respect to its solid decomposition products.

REFERENCES

1. E. Chauvenet, Contribution A., L-Etude des Derives Halogens et Oxy-Halogens du Thorium, Ann. Chem. Phys. 23, 425 (1911)

2 R. W. M. D'Eye, "The Thorium Dioxide - Thorium Tetrafluoride System," J. Chem. Soc. Part I, 1958, p. 196

3. N. W. Gregory, "The $UOBr_2$ Disproportionation Equilibrium," U. S. Atomic Energy Comm. Report BC-18 (1946)

4. J. J. Katz and E. Rabinowitch, The Chemistry of Uranium, (McGraw-Hill Book Co., Inc. New York 1951)

5. J. P. Coughlin, "Contributions to the Data on Theoretical Metallurgy, XII Heats and Free Energies of Formation of Inorganic Oxides," U. S. Bureau of Mines Bull 542 (1954)

6. A. J. Darnell and F. J. Keneshea, Jr., "Vapor Pressure of Thorium Tetrafluoride," J. Phys. Chem., 62 (1958), p. 1143

7. A. J. Darnell, "The Free Energy, Heat, and Entropy of Formation of Thorium Tetrafluoride," NAA-SR-4924, Feb. 15, 1960

8. G. E. Moore and K. K. Kelley, "High-Temperature Heat Contents of Uranium, Uranium Dioxide, and Uranium Trioxides," J. Am. Chem. Soc. 69 (1947), p. 2105

9. D. C. Ginnings and R. J. Corruccini, "Heat Capacities at High Temperatures of Uranium, Uranium Trichloride, and Uranium Tetrachloride," J. Research Natl. Bur. Standards 39 (1947), p. 309-16

10. E. Greenberg and E. F. Westrum, Jr., "Heat Capacity and Thermodynamic Functions of Uranium (IV) Oxychloride and Uranium (IV) Oxybromide from 10 to 350°K," J. Am. Chem. Soc. 78 (1956), p. 5144