NAA-SR-4924
CHEMISTRY-GENERAL
13 PAGES

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

By
A. J. DARNELL

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: FEBRUARY 15, 1960

DISTRIBUTION

This report has been distributed according to the category "Chemistry-General" as given in "Standard Distribution Lists for Unclassified Schientific and Technical Reports" TID-4500(15th Ed.), August 1, 1959. A total of 525 copies was printed.

This report has been accepted for publication by J. Inorg. and Nuclear Chem.

CONTENTS

TABLES

FIGURES

ABSTRACT

The equilibrium constant for the reaction, $ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$ was determined over the temperature interval 871 to 1077°K by measuring the equilibrium pressure of SiF_4 above the system. The pressure of SiF_4 from this reaction is given by $\log P_{(atm)} = \frac{-8200 \pm 120}{T\ (°K)} + 7.740 \pm 0.130$. A heat capacity correction of -2.76 cal/deg-mole gives, for the reaction at 298°K: $\Delta F° = 27.9$ kcal/mole, $\Delta H° = 39.4$ kcal/mole, and $\Delta S° = 38.7$ cal/deg-mole. From these and existing thermodynamic data for SiO_2, ThO_2, and SiF_4 the $\Delta F°$, $\Delta H°$, and $\Delta S°$ of formation of ThF_4 from the elements at 298°K were calculated to be -459.9 kcal/mole, -482.4 kcal/mole, and -75.8 cal/deg-mole, respectively.

ACKNOWLEDGMENT

The author wishes to express appreciation to Dr. S. J. Yosim and Dr. D. E. McKenzie for many helpful discussions and to Mr. W.A. McCollum for assistance in carrying out the experimental work.

I. INTRODUCTION

The reaction of metal fluorides with silica has been previously noted by several workers.[1, 2, 3] In earlier work by the author,[4] it was observed that thorium tetrafluoride reacted with quartz at elevated temperatures to form SiF_4 gas. The present study showed that a reversible reaction occurred between thorium tetrafluoride and silica and the products, silicon tetrafluoride, and thorium dioxide. The equilibrium constant was determined by measuring the pressure of SiF_4 above the system at equilibrium. The derived thermochemical constants for this reaction were combined with the published thermochemical properties of ThO_2,[5] SiO_2,[5] and SiF_4[6] to obtain $\Delta F°$, $\Delta H°$, and $\Delta S°$ of formation of solid ThF_4.

II. EXPERIMENTAL

A. MATERIALS

Thorium tetrafluoride was obtained from the A. D. Mackay Company. This material initially contained 0.2 wt % volatile impurities, most of which was water. The salt was purified by heating under vacuum at 600°C for 16 hr to remove the volatile impurities. Analysis then showed 75.3 wt % Th and 25.4 wt % F (theoretical, 75.33 wt % thorium and 24.67 wt % fluorine). Silicon dioxide was prepared by reacting C.P. grade silicon tetrafluoride with water. The precipitate was washed, filtered, and then fired at 800°C until a constant weight was obtained. This process gave fine particles of SiO_2 powder which reacted more rapidly with ThF_4 than commercially available SiO_2. Thorium dioxide of 99.8 wt % purity was obtained from Rare Earths Incorporated; it was heated in vacuo at 700°C for a period of sixteen hour before use.

Samples for the equilibrium studies were prepared by thoroughly mixing together equimolar quantities of powdered ThF_4 and SiO_2, then compressing this mixture into pellets with a hydraulic press at a pressure of 2 tons/in.^{2}. These pellets were then broken into approximately 1 mm cubes. Mixtures prepared in this manner reacted satisfactorily to give equilibrium pressures of SiF_4 in from 2 to 4 hour. Less thorough mixing resulted in slower reaction rates which required from 1 to 5 days to attain equilibrium.

B. APPARATUS AND PROCEDURE

The pressure of SiF_4 above the solid reactants was measured by use of the manometric technique. The solid reaction mixture, ThF_4 and SiO_2, was placed in a quartz reaction cell surrounded by a nickel thermal shield to minimize thermal gradients. This assembly was placed in a tube furnace maintained at a constant temperature (± 2°C) by a potentiometric type regulator. The temperature of the reaction was measured by a calibrated Pt-Pt 90%, Rh 10% thermocouple placed in a well in the quartz cell. The reaction cell was connected to a mercury manometer by a 6 mm quartz tube packed with quartz wool to reduce thermal convection in the system. This apparatus was connected to a vacuum system, gas sampling bulb, and inlet for introducing SiF_4 into the cell.

Measurements of SiF_4 equilibrium pressures were made by the following procedures: The system was evacuated at room temperature, then at 400°C for one hour to remove adsorbed impurities. The system was then sealed off at the vacuum pump, the reaction cell was raised to the desired temperature, and the pressure of SiF_4 was measured by means of the mercury manometer. Pressure readings were taken until there was no further change in pressure with time.

III. RESULTS AND DISCUSSION

Equilibrium pressures of SiF_4 obtained from the reaction of ThF_4 and SiO_2 are shown in Table I.

TABLE I

EQUILIBRIUM PRESSURES OF SiF_4 FOR THE REACTION

$ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$

Temperature (°K)	P_{SiF_4} (atm)	Temperature (°K)	P_{SiF_4} (atm)
Equilibrium approached from lower pressures.		1000	0.318
		1038	0.651
871	0.020	1076	1.289
882	0.034	1077	1.260
886	0.026	Equilibrium approached from higher pressures.	
935	0.085		
937	0.097	884	0.038
945	0.114	936	0.094
960	0.154	1030	0.660
985	0.245	1054	1.200
995	0.290		

SiF_4 was identified as the gaseous product of the reaction by chemical and mass spectrographic analysis of gas samples taken from the reaction cell. Room temperature X-ray diffraction analyses of samples quenched from equilibrium, in which 70 mole % of the fluorine had been converted to SiF_4, showed that the major solid product was thorium dioxide.[7] Under forcing conditions, i.e., by removal of SiF_4 by condensation on a cold finger, equimolar amounts of ThF_4 and SiO_2 reacted essentially quantitatively (>99%) to ThO_2 and SiF_4. The overall reaction can thus be represented by

$$ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g) \quad . \qquad \ldots(1)$$

Further studies were made to determine if Reaction 1 represents the solid phases in the equilibrium since the X-ray diffraction patterns of quenched samples showed traces of thorium oxyfluoride.[8] D'Eye[8] reports that ThF_4 and ThO_2 react at 900-1000°C to form $ThOF_2$. Tests carried out on the reverse of Reaction 1, by reacting SiF_4 with pure ThO_2, yielded equilibrium pressures which were in good agreement with those obtained from the forward reaction (see Table II). This indicated that the phases in the equilibrium were as shown in Reaction 1. In addition, reaction of $ThOF_2$* and SiO_2 gave equilibrium pressures of SiF_4 which were lower than the pressures yielded by the reaction of ThF_4 and SiO_2.

TABLE II

EQUILIBRIUM PRESSURES OF SiF_4 FOR THE REACTION

$SiF_4(g) + ThO_2(s) \rightleftharpoons ThF_4(s) + SiO_2(s)$

Temperature (°K)	P_{SiF_4} (atm)
923	0.073
1043	0.659

The solid solution of ThF_4 in ThO_2, to the extent of 25 mole % ThF_4 at 1000°C found by D'Eye,[8] probably does not occur to an appreciable extent at the lower temperatures of this investigation since the equilibrium pressures of SiF_4 from Reaction 1 and from the reverse of Reaction 1 were essentially constant (at constant temperature) over the entire composition range. Therefore, the activities of the solid phases were apparently the same whether the solid phases ThO_2 and ThF_4 or SiO_2 were in excess.

The agreement of the final pressures of SiF_4, when approached from zero pressure and from pressures above the equilibrium pressure, offers good

---

*$ThOF_2$ prepared by method of D'Eye.[8]

evidence that chemical equilibrium was attained. Figure 1 shows the pressure of SiF_4 vs time for Reaction 1, starting from zero pressure and from 0.2 atm SiF_4. Similar experiments were carried out at 884, 1030, and 1054°K; the results are shown in Table I and Figure 2.

The activities of the solid phases in Reaction 1 were considered to be unity for the following thermodynamic calculations. Assuming that SiF_4 behaves as an ideal gas, the equilibrium constant for Reaction 1 may be expressed as,

$$K = P_{SiF_4} \qquad \ldots(2)$$

A least squares analysis was made of the P_{SiF_4} data in Tables I and II. The pressure of SiF_4 as a function of temperature is:

$$\log P_{SiF_4}\,(\text{atm}) = \frac{-8200 \pm 120}{T°K} + 7.740 \pm 0.130, \quad (871\text{-}1077°K)\,. \qquad \ldots(3)$$

The enthalpy of the reaction is obtained from the van't Hoff equation. At the mid-temperature of the experimental range (974°K), $\Delta H°$ (reaction) = + 37.5 ± 0.5 kcal/mole. The ΔCp of Reaction 1 is -2.76 cal/deg-mole at 298°K (see Table III). It is assumed that ΔCp is constant from 298 to 974°K, since there are no high temperature heat capacity data for ThF_4. Then $\Delta F°_T$ for Reaction 1 is:

$$\Delta F°_T = 40{,}210 + 6.36\,T \log T - 57.19T \qquad \ldots(4)$$

The following results are calculated for the reaction at 298°K:

$$\Delta F° = 27.9 \text{ kcal/mole} \qquad \ldots(5)$$

$$\Delta H° = 39.4 \text{ kcal/mole} \qquad \ldots(6)$$

$$\Delta S° = 38.7 \text{ cal/deg-mole} \qquad \ldots(7)$$

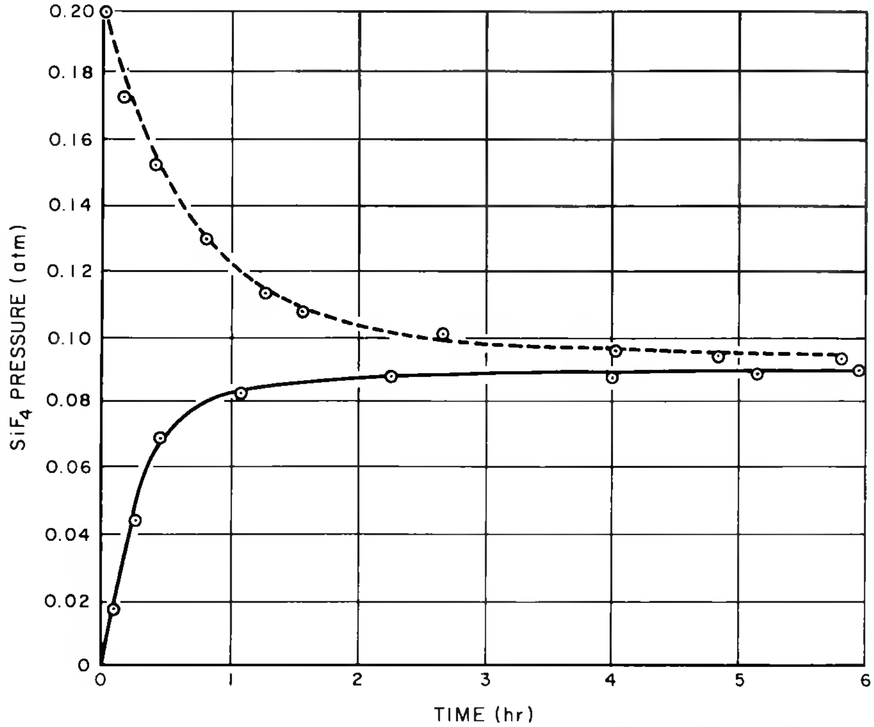

Figure 1. Pressure vs Time at 936°K for the Reaction $ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$

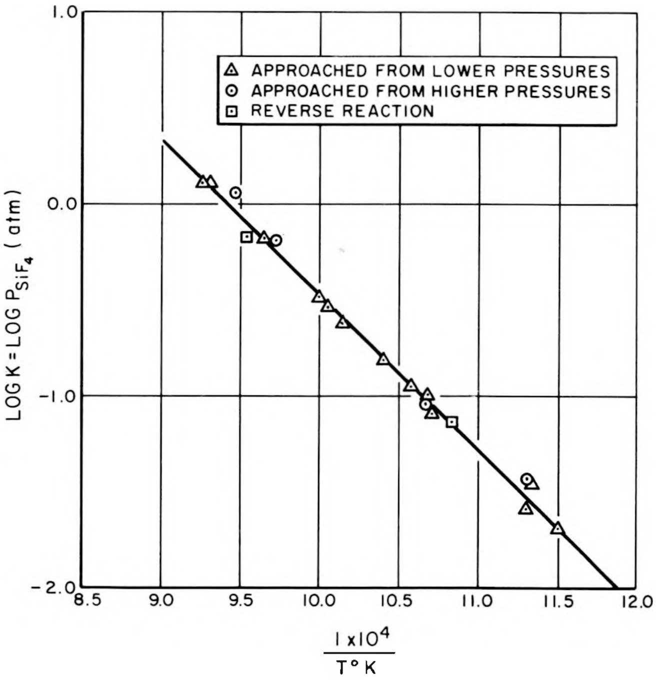

Figure 2. Equilibrium Constant vs 1/T for the Reaction $ThF_4(s) + SiO_2(s) \rightleftharpoons ThO_2(s) + SiF_4(g)$

The above data were combined with published thermochemical data for $ThO_2(s)$, $SiO_2(s)$, and $SiF_4(g)$ (Table III), to obtain the free energy, enthalpy, and entropy of formation of $ThF_4(s)$ from the elements in their standard states at 298°K. This yields

$$\Delta F^\circ = -459.9 \text{ kcal/mole} \qquad \ldots(8)$$

$$\Delta H^\circ = -482.4 \text{ kcal/mole} \qquad \ldots(9)$$

$$\Delta S^\circ = -75.8 \text{ cal/deg-mole} \qquad \ldots(10)$$

TABLE III
THERMODYNAMIC DATA

	$\Delta H^\circ_{298}(f)$ $\left(\frac{kcal}{mole}\right)$	$\Delta F^\circ_{298}(f)$ $\left(\frac{kcal}{mole}\right)$	$\Delta S^\circ_{298}(f)$ $\left(\frac{cal}{deg\text{-}mole}\right)$	S°_{298} $\left(\frac{cal}{deg\text{-}mole}\right)$	Cp°_{298} $\left(\frac{cal}{deg\text{-}mole}\right)$
$ThO_2(s)$	-293.2± 0.4[*]	-279.2[*]	-47.0	-	14.76[†]
$SiF_4(g)$	-359.7± 2.8[§]	-349.7	-33.7	67.77[**]	17.56[**]
$SiO_2(\alpha\text{-quartz})$	-209.9± 1.0[*]	-196.9[*]	-43.6	-	10.62[§§§]
Reaction:					
$ThF_4(s) + SiO_2(quartz) \rightleftharpoons ThO_2(s) + SiF_4(g)$					
	39.4± 0.5[††]	27.9[††]	38.7[††]	-	$\Delta Cp = -2.76$
ThF(s)	-482.4± 3.5[††]	-459.9[††]	-75.8[††]	33.9[††]	-
$ThF_4(s)$	-477[§§]	-454[§§]	-76[§§]	(estimate by L. Brewer)	
Th(s)	-	-	-	12.76[***]	-
$2F_2(g)$	-	-	-	96.90[***]	-
$ThF_4(s)$	-	-	-	33.9[†††]	26.46[†††]

*See Reference 5
†See Reference 11
§See Reference 12
**See Reference 13
††This Work
§§See Reference 6
***See Reference 9
†††See Reference 10
§§§See Reference 14

The absolute entropy of $ThF_4(s)$, obtained from the above ΔS°_{298} of formation of $ThF_4(s)$ and S°_{298} of Th(s)[9] and $F_2(g)$[9] (see Table III), is 33.9 cal/deg-mole. Lohr, Osborne, and Westrum[10] report S°_{298} = 33.9 cal/deg-mole from low temperature heat capacity measurements on thorium tetrafluoride.

It is pointed out that this equilibrium method inherently has the combined uncertainties of the thermodynamic properties of ThO_2, SiO_2, and SiF_4 in addition to the uncertainty of this measurement. The uncertainty in $\Delta H^\circ_{298}(ThF_4)$ is estimated to be ± 3.5 kcal/mole.

The equilibrium between a metal oxide and metal fluoride offers a convenient method for determining the thermodynamic properties of a metal fluoride which is not amenable to measurements by calorimetric or electromotive force methods.

REFERENCES

1. J. W. Mellor, Comprehensive Treatise of Inorganic and Theoretical Chemistry (Longmans, Green and Co.), 1952
2. Joseph J. Katz and Eugene Rabinowitch, The Chemistry of Uranium (McGraw-Hill Book Co.), 1951
3. M. V. Smirnov and L. E. Ivanowskii, "Reaction of Thorium Oxide with its Chloride in Molten Salt Solution," Zhur. Neorg. Khim., 1, 1843-49 (1956).
4. A. J. Darnell and F. J. Keneshea, Jr., "Vapor Pressure of Thorium Tetrafluoride," J. Phys. Chem. 68, 1143 (1958)
5. James 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. L. L. Quill, Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, (McGraw-Hill Book Co., New York) 1950
7. H. E. Swanson and E. Tatge, Standard X-ray Diffraction Patterns, (National Bureau of Standards) Circ. 539. 1. p 57 (1953)
8. R. W. M. D'Eye, "The Thorium Dioxide - Thorium Tetrafluoride System," J. Chem. Soc., 1958; 196-199
9. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Am. Chem. Soc. (1956)
10. H. R. Lohr, D. W. Osborne, and E. F. Westrum, Jr., "Thermodynamic Properties of Thorium Tetrafluoride from 5 to 300°K," J. Am. Chem. Soc. 76, 3837-39 (1954)
11. J. C. Southard, "A Modified Calorimeter for High Temperatures. The Heat Content of Silica, Wollastonite and Thorium Dioxide above 25°," J. Am. Chem. Soc., 63, 3142 (1941)
12. H. von Wartenberg and R. Schutte, "The Heat of Formation of SiF_4, CF_4, and SiC," Z. anorg. allgem. Chem., 211, 222 (1933)
13. F. L. Voelz, A. G. Meister, and F. F. Cleveland, "Force Constants and Calculated Thermodynamic Properties for Silicon Tetrafluoride," J. Chem. Phys. 19, 1084 (1951)
14. C. T. Anderson, "The Heat Capacities of Quartz, Cristobalite and Tridymite at Low Temperatures," J. Am. Chem. Soc. 58, 568 (1936)