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High-Temperature Enthalpy and X-Ray Powder Diffraction Data for ZrI_4

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLES

HIGH-TEMPERATURE ENTHALPY AND X-RAY POWDER DIFFRACTION DATA FOR ZrI_4

by

M. J. Ferrante[1] and R. A. McCune[1]

ABSTRACT

New data on zirconium tetraiodide (ZrI_4) have resulted from high-temperature enthalpy and X-ray powder diffraction studies conducted by the Bureau of Mines. These studies were undertaken as part of the Bureau's efforts to provide important thermodynamic data essential to the advancement of mineral resources technologies that can be employed with minimal energy requirements and minimal environmental degradation. Enthalpies were measured with a copper-block drop calorimeter. No transitions or other anomalies were found. Tabulated values are given from 298.15 to 772 K for relative enthalpy, heat capacity, entropy, and Gibbs energy function. Enthalpies are expressed in equation form and combined with data from the literature to calculate values of the standard enthalpy of formation and the Gibbs energy of formation. X-ray powder diffraction data indicate that ZrI_4 is primitive cubic with a lattice parameter of 11.79 A and is isostructural with stannic iodide (SnI_4).

INTRODUCTION

Zirconium alloys are used extensively in commercial applications as sheaths for fuel rods in nuclear reactors. Unfortunately, the sheaths sometimes fail (by cracking). A probable explanation for the failure is the stress-corrosion cracking caused by fission products such as iodine, as described by Cox (3)[2]. The mechanism of this stress-corrosion cracking is not fully understood, but presumably involves reactions between zirconium and iodine. To better understand the zirconium-iodine system, studies by the Bureau of Mines were made on ZrI_4 to measure the high-temperature enthalpies relative to 298.15 K, and to establish its powder diffraction and crystallographic data. This investigation is an essential part of the Bureau of Mines overall goal of maintaining an adequate supply of minerals to meet national economic and strategic needs.

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[1]Research chemist, Albany Research Center, Bureau of Mines, Albany, Oreg.
[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The investigation of high-temperature enthalpies was made with a drop calorimeter incorporating a copper block. Although the resulting enthalpy values were recently published by Cubicciotti (4), the additional work described here was done to provide values for ΔHf°_{298}, ΔGf°, and X-ray powder diffraction data for $ZrI_4(c)$[3]. X-ray powder diffraction studies were made with a high-angle, vertical diffractometer.

MATERIALS

To prepare ZrI_4 for this investigation, zirconium that was 99.9+ pct pure was reacted with reagent-grade iodine[4]. A stoichiometric mixture of zirconium and iodine, plus a 10-pct excess zirconium, was vacuum sealed in a Pyrex[5] tube and gradually heated to approximately 760 K in a tilted tubular furnace. The temperature was maintained for 10 hours. Then the top portion of the tube was withdrawn from the furnace and allowed to air cool to condense the ZrI_4. The tube was opened in a dry box under an argon atmosphere, and a ZrI_4 sample was sealed in an evacuated glass bulb for shipment to the Bureau of Mines at Albany, Oreg. The bulb was then opened in a dry box under an argon atmosphere, and the lump of ZrI_4 was ground with a mortar and pestle. Powdered samples were used for enthalpy measurements, X-ray diffraction, and chemical analyses. Chemical analyses showed 15.15 pct Zr and 84.85 pct I compared with the theoretical composition of 15.23 pct Zr and 84.77 pct I. Optical emission spectroscopy revealed that the iodide contained less than 0.01 pct metallic impurities, including hafnium.

EXPERIMENTAL WORK AND RESULTS

Enthalpies Above 298.15 K

High-temperature enthalpies were measured with a copper-block calorimeter, as described by Douglas (5), although the calorimeter used in this study incorporated a more sensitive potentiometric system. The copper block has a heat capacity of about 1.51 kcal/degree. The resistance thermometer, a transposed-bridge type as described by Maier (11), is wound around the copper block. Before and after the enthalpy measurements of each substance, the calorimeter was calibrated electrically, and the entire system was checked by measuring the enthalpy of pure magnesium oxide (MgO). These MgO measurements agreed within 0.1 pct of the values reported by Victor (16). Enthalpy measurements are expressed in terms of the thermochemical calorie with 1 cal = 4.1840 j.

A clear glass capsule of pure silica was the sample container for experimental measurements. Enthalpies of the empty capsule were measured in separate experiments and constituted about 50 pct of the total for the capsule plus ZrI_4 sample. The empty capsule had an internal volume of

[3]Letter c indicates crystalline form.
[4]ZrI_4 used in this research was supplied by D. Cubicciotti of the Stanford Research Institute, Menlo Park, Calif.
[5]Reference to a specific brand name is made for identification only and does not imply endorsement by the Bureau of Mines.

6.21 cm^3. The capsule was filled with powdered ZrI_4 in the dry box, and then transferred to a vacuum system without exposure to air. The neck of the evacuated capsule was sealed with a flame while the portion of the capsule containing the ZrI_4 was immersed in ice water.

The sample mass of ZrI_4 was 17.3459 grams. Mass was periodically checked for constancy by weighing the ZrI_4 and capsule together between enthalpy measurements. All weighings were corrected to vacuum. The molecular weight of 598.838 for ZrI_4 conforms to the 1977 Table of Atomic Weights (8).

The temperature of the ZrI_4 and the capsule in the furnace was measured with a platinum-10 pct rhodium versus platinum thermocouple, which was frequently calibrated against the melting point of pure gold. The temperatures of the experimental measurements refer to the International Practical Temperature Scale of 1968 (2).

The results of experimental values for $H°-H°_{298}$ are listed in table 1. The measurements at the two highest temperatures were corrected for vaporization of the ZrI_4 inside the sealed capsule, by 0.09 pct at 653.2 K and by 0.37 pct at 703.1 K. The method used for vapor correction was described by Douglas. The vapor pressure and enthalpy of vaporization were calculated from Cubicciotti's measurements. Enthalpy measurements were discontinued at 703.1 K, because Cubicciotti showed that vapor pressure increases rapidly as temperature nears the melting point of 772 K. This melting point was adopted from the work of Rahles (13). The X-ray diffraction pattern of ZrI_4 removed from the capsule after completion of the enthalpy measurements was the same as the pattern of the starting substance.

TABLE 1. - High-temperature experimental enthalpies of ZrI_4(c)

T, K	$H°-H°_{298}$, kcal/mole	T, K	$H°-H°_{298}$, kcal/mole	T, K	$H°-H°_{298}$, kcal/mole
403.1........	3.182	503.0........	6.259	602.8........	9.409
453.2........	4.725	503.1........	6.273	[1]653.2........	11.002
502.9........	6.262	552.7........	7.829	[2]703.1........	12.592

[1]Measurement is corrected for ZrI_4 vaporization (0.09 pct less than original measurement).
[2]This measurement is also corrected for ZrI_4 vaporization (by 0.37 pct).

X-ray Powder Diffraction Procedure

The powdered sample of ZrI_4 for X-ray diffraction was double bottled in the argon-filled glove box and delivered to the diffraction laboratory, where the bottle was opened in a glove box filled with helium. A flat sample holder was loaded by pressure packing from the top, placed on a diffractometer spindle, and covered with a gastight cap fitted with a 2-mil-thick Mylar window. The spindle, sample, and cap were removed from the glove box and positioned on the diffractometer. An identification scan was made with nickel-filtered copper radiation at 45 kv and 35 ma. A scintillation detector was used with pulse-height discrimination, solid-state electronics, and a strip-chart recorder. The diffractometer scan rate for identification was at

1° 2θ/min while the chart speed was 1/2 in/min. The diffraction pattern, d-spacing, and relative intensities obtained for ZrI_4 and SnI_4 are given in table 2, along with the calculated lattice parameters and the reflecting planes.

TABLE 2. - X-ray diffraction patterns of ZrI_4 and SnI_4

hkl	[1]ZrI_4			[2]SnI_4	
	d, A	I	a_o, A[3]	d, A	I
111.............	6.79	12	11.78	7.09	3
102.............	5.26	6	11.76	5.49	10
211.............	NO	NO	NO	5.012	15
222.............	3.401	100	11.78	3.543	100
302.............	NO	NO	NO	3.404	5
400.............	2.948	53	11.79	3.070	32
331.............	NO	NO	NO	2.816	3
421.............	2.575	2	11.80	2.678	6
332.............	NO	NO	NO	2.617	5
502.............	NO	NO	NO	2.279	5
521.............	2.160	1	11.83	2.241	4
440.............	2.084	44	11.79	2.1701	41
622.............	1.780	8	11.80	1.8503	26
631.............	NO	NO	NO	1.8097	6
444.............	1.704	25	11.80	1.7717	2
702.............	NO	NO	NO	1.6862	2
721.............	NO	NO	NO	1.6701	<1
732.............	NO	NO	NO	1.5587	5
800.............	1.475	2	11.80	1.5345	11
662.............	NO	NO	NO	1.4074	3
832.............	NO	NO	NO	1.3983	2
840.............	1.320	3	11.80	1.3720	4

NO Diffraction lines were not observed.
[1]Measurements from the present investigation.
[2]Measurements by Swanson (15).
[3]Average a_o = 11.79±0.02 A.

DISCUSSION

Enthalpy Study of ZrI_4

The thermal behavior of ZrI_4 showed no transitions or other anomalies. No low-temperature heat capacities were found in the literature to merge with the high-temperature enthalpies of the present investigation. The experimental enthalpies were computer fitted with smooth curves, using polynamial functions as described by Justice (9). The resulting smoothed values of enthalpy relative to 298.15 K and related thermodynamic properties of $C_p°$, $S°-S°_{298}$ increment, and $-(G°-H°_{298})/T$ are shown in table 3. The uncertainty of the smoothed enthalpies is estimated to be ±0.4 pct. The standard error of measurement was 0.1 pct. The relationship between the smoothed and experimental enthalpies is shown graphically in figure 1 as the mean heat capacity $(H°-H°_{298})/(T-298.15)$.

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$$[-(G^\circ-H^\circ_{298})/T] - S^\circ_{298}$$

TABLE 3. - High-temperature thermodynamic properties of $ZrI_4(c)$

T, K	Cal/deg-mole			$H^\circ-H^\circ_{298}$, kcal/mole
	C_p°	$S^\circ-S^\circ_{298}$	$-(G^\circ-H^\circ_{298})/T$	
298.15	29.90	0	0	0
300	29.92	.185	.002	.055
350	30.32	4.83	.36	1.563
400	30.63	8.90	1.18	3.087
450	30.91	12.53	2.25	4.625
500	31.16	15.79	3.44	6.177
550	31.39	18.78	4.71	7.740
600	31.61	21.52	5.99	9.316
650	31.83	24.05	7.28	10.900
700	32.04	26.42	8.56	12.500
750	[1](32.25)	(28.64)	(9.83)	(14.105)
772[2]	(32.34)	(29.57)	(10.38)	(14.815)

[1]Values in parentheses are extrapolations.
[2]Melting point of ZrI_4.

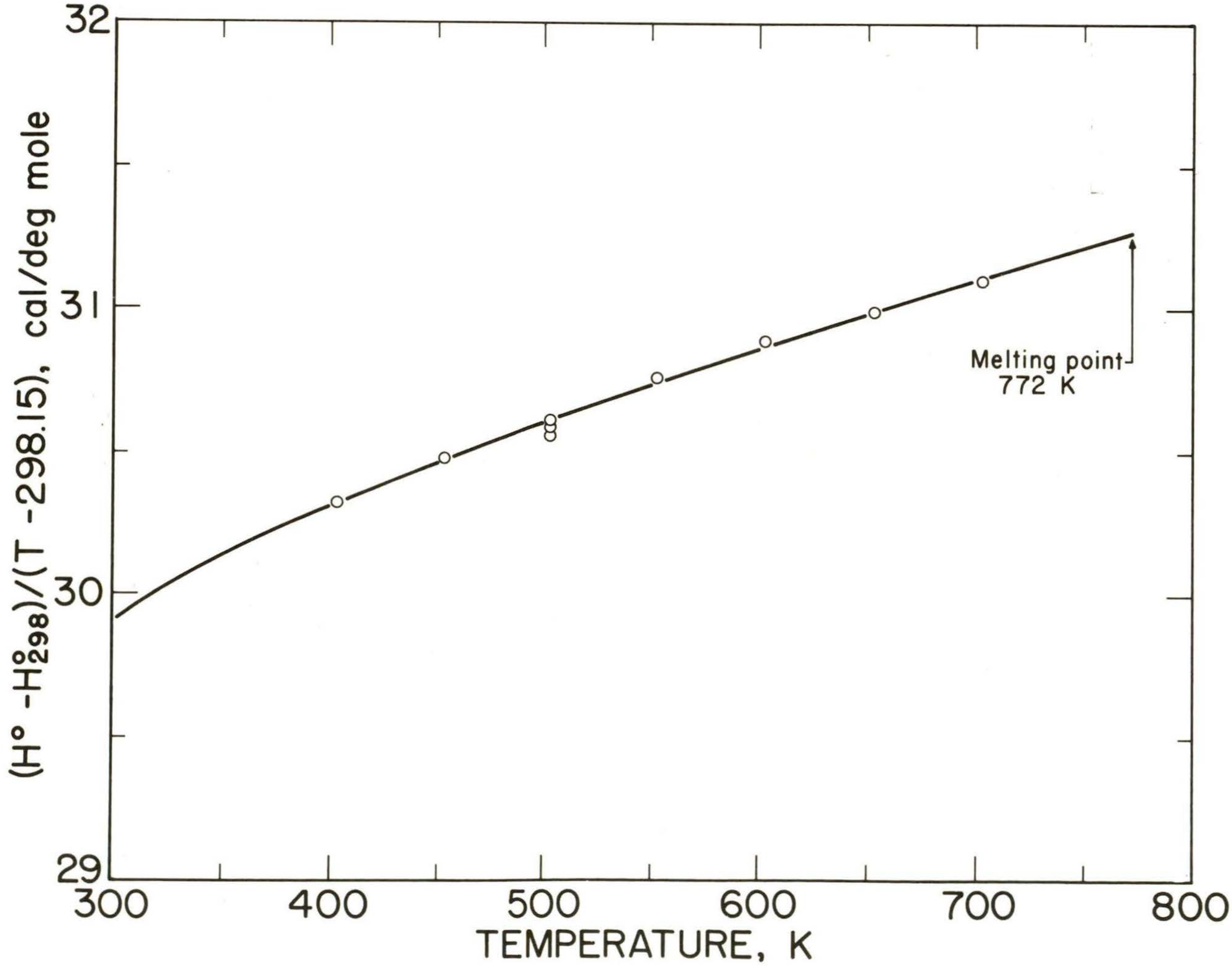

FIGURE 1. - High-temperature mean heat capacities of $ZrI_4(c)$.

The smoothed enthalpies were also expressed by the standard-form equation to better meet the needs of engineering applications. Kelly (10) described the method of derivation of the equation, which was based on the form of Maier (12) and on the graphical procedure developed by Shomate (14). The derived equation is expressed in kilocalories per mole. The temperature range of validity and the average deviation from the experimental data are shown in the parentheses after the following equation:

$$H°-H°_{298} = 29.498 \times 10^{-3}T + 1.906 \times 10^{-6}T^2 + 62.3T^{-1} - 9.173$$

(298 - 772 K, 0.05 pct)

This equation is an excellent fit to the smoothed enthalpies, with an average deviation of 0.005 pct. Consequently, not much accuracy is lost in using enthalpies calculated from the equation instead of the enthalpies from table 2.

Enthalpy values of the present investigation were combined with supplementary thermodynamic data from the literature to calculate the ΔHf°, ΔGf°, and log KF; these values are shown in table 4. All supplementary data for zirconium(c) were taken from Hultgren (7). Similar information for crystalline, liquid, and gaseous iodine (c,l,g) was obtained from the JANAF tables (6). $\Delta Hf°_{298}$ for ZrI_4(c) was also obtained from JANAF (1). The absolute entropy of ZrI_4(c) at 298.15 K is 59.8±0.2 cal/deg-mole and was calculated from Cubicciotti's vapor pressure measurements combined with enthalpy measurements from the present investigation.

TABLE 4. - Formation data for $Zr(c) + 2I_2(c,l,g) = ZrI_4(c)$

T, K	Kcal		Log Kf	T, K	Kcal		Log Kf
	ΔHf°	ΔGf°			ΔHf°	ΔGf°	
298.15......	-116.80	-115.30	84.517	458.4.......	-145.64	-112.92	53.836
300.........	-116.80	-115.29	83.989	500.........	-145.37	-109.96	48.068
386.8[1]......	-117.14	-114.81	64.870	600.........	-144.72	-102.95	37.500
386.8.......	-124.56	-114.81	64.870	700.........	-144.04	-96.03	29.982
400.........	-124.75	-114.48	62.549	772[3]........	-143.55	-91.12	25.796
458.4[2]......	-125.59	-112.92	53.836				

[1]Melting point of I_2.
[2]Boiling point of I_2.
[3]Melting point of ZrI_4.

X-Ray Powder Diffraction Study of ZrI_4

The X-ray powder diffraction studies reveal that the structure of ZrI_4 primitive cubic with a lattice parameter of 11.79±0.02 A. The powder diffraction pattern for ZrI_4 has a marked similarity to the powder diffraction pattern for SnI_4 given in table 2 for comparison. ZrI_4 is probably isostructural with SnI_4, which is listed by Wyckoff (17) as a structure type and is in space group No. 205, T_h^6 - Pa3, with eight formula units per unit cell. The density of ZrI_4, calculated from the lattice constant, is 4.85 g/cm^3 at 26° C.

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