[CONTRIBUTION FROM SOUTHERN EXPERIMENT STATION, REGION V, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR AND THE SCHOOL OF CHEMISTRY, UNIVERSITY OF ALABAMA]

High Temperature Heat Content and Entropies of Hafnium Tetrafluoride and Rubidium Fluoride[1]

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Measurements of heat contents above 273°K. were conducted for hafnium tetrafluoride and rubidium fluoride to temperatures of 1103 and 1199°K., respectively. Normal behavior was observed for both compounds. Heat content equations were derived and entropies calculated.

Introduction

This paper presents the results of heat-content measurements throughout the temperature range 273.15 to 1199.0°K., with calculated entropies for hafnium tetrafluoride and rubidium fluoride.

Data on these compounds in the range studied have not been published previously.

Materials

The hafnium tetrafluoride (supplied by the Oak Ridge National Laboratories) was purified by sublimation under vacuum. Thereafter, spectrographic analysis[2] showed these impurities: Zr, 1.0%, with traces of Mg, Al, V and Fe. The experimental results reported have not been corrected for impurities.

The rubidium fluoride (also supplied by the Oak Ridge National Laboratories) was used as received. Impurities, determined spectrographically,[2] were KF, 0.2%, NaF, 0.0001%.

The samples were enclosed in platinum crucibles, the heat contents of which were determined by separate measurements. After filling with sample, the crucibles were evacuated, filled with helium, evacuated to approximately 10 mm. helium pressure and sealed by platinum welding.

Measurements and Results

Heat-content measurements were made in a Bunsen ice calorimeter of the type described in detail by Ginnings and Corruccini.[3] The calibration factor for the unit, established electrically, was found to be 270.44 ± 0.06 joules per gram of mercury. Additional calibration tests on a synthetic sapphire sample, at four different temperatures, yielded enthalpy values that checked accepted values[4] with less than 0.15% deviation.

The experimental procedure used in the calorimetric studies was as follows: A sample of approximately 18 g., sealed in the platinum container, was heated to an approximate predetermined temperature in a Marshal furnace designed so that it could be shunted to obtain a region of uniform temperature. The temperature of the furnace was measured with a platinum–platinum 10% rhodium thermocouple previously calibrated against a National Bureau of Standards thermocouple. Once it had been assured that the entire sample and container had reached the test temperature, the container was dropped into the calorimeter, the system closed and the heat evolved in cooling to 273.15°K. measured with the greatest possible accuracy. This procedure was repeated at temperature intervals of approximately 30° over the 273.15 to 1199.0°K. range. In each run the previously determined heat content of the container for that temperature was deducted from the total heat evolved.

The experimentally determined heat-content values of the samples are listed in Table I. They are expressed in calories per mole and the molecular weights are in accord with the 1953 International Atomic Weights.

TABLE I

MEASURED HEAT CONTENTS ABOVE 273.15°K. (CAL. MOLE^{-1})

T, °K.	$H_T - H_{273.15}$	T, °K.	$H_T - H_{273.15}$
	RbF (mol. wt. 104.48)		
372.2	1253	719.8	5954
384.4	1338	756.9	6399
398.5	1528	775.1	6690
406.7	1642	806.6	7203
423.2	1913	816.9	7245
443.9	2101	835.8	7586
459.1	2290	870.3	8110
476.9	2560	911.6	8914
488.2	2723	945.8	9536
517.9	3111	964.7	9711
555.4	3629	991.3	10234
566.4	3676	1018.4	10656
594.5	4095	1034.2	11160
620.2	4420	Liquid	
637.7	4637	1075.6	17274
651.7	4844	1106.8	17855
678.9	5198	1136.2	18383
709.0	5536	1167.4	18896
716.5	5829	1199.0	19349
	HfF_4 (mol. wt. 254.6)		
365.7	2190	697.5	11729
388.8	2939	704.5	11936
424.2	4011	722.5	12606
459.5	4743	762.8	14002
482.4	5449	815.8	15535
494.5	6011	822.0	15677
514.6	6527	839.6	16284
550.8	7365	869.6	17372
572.8	8015	874.6	17522
578.2	8181	891.9	18039
609.1	9100	913.7	18537
626.6	9657	944.3	19362
657.3	10437	971.5	20383
663.6	10649	1008.6	21551
674.8	11080	1041.0	22615
688.5	11478	1078.4	23696
		1103.3	24591

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(1) (a) Work on manuscript completed October 1958. (b) The work upon which this report is based was carried out in coöperation with the University of Alabama.

(2) E. E. Creitz, supervisory chemist, analytical, Bureau of Mines Southern Experiment Station, Tuscaloosa, Ala.

(3) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583 (1947).

(4) D. C. Ginnings and G. T. Furukawa, THIS JOURNAL, **75**, 522 (1953).

Hafnium tetrafluoride did not exhibit any phase changes within the range of temperatures studied. Equipment limitations prevented extending the heat-content measurements to a temperature sufficiently high for determining the melting point and the heat of fusion of this compound.

Rubidium fluoride had one phase change, that of melting, within the temperature range studied. The results for this compound, in both solid and liquid states, appear normal in comparison with other alkali halides. The melting point was found to be 1048°K. and the heat of fusion 5490 cal. per mole.

TABLE II

HEAT CONTENTS (CAL. MOLE^{-1}) AND ENTROPY INCREMENTS (CAL. DEGREE^{-1} MOLE^{-1}) ABOVE 273.5°K.

	RbF		HfF_4	
T, °K.	$H_T - H_{273.15}$	$S_T - S_{273.15}$	$H_T - H_{273.15}$	$S_T - S_{273.15}$
298.15	305	1.06	675	1.86
400	1544	4.65	3276	9.33
450	2175	6.14	4621	12.49
500	2823	7.50	6023	15.44
550	3489	8.77	7344	17.96
600	4175	9.96	8832	20.54
650	4881	11.06	10344	22.92
700	5609	12.14	11886	25.20
750	6356	13.17	13431	27.33
800	7148	14.19	14990	29.34
850	7912	15.17	16565	31.35
900	8723	16.10	18147	33.15
950	9553	17.00	19717	34.84
1000	10408	17.88	21321	36.48
1048	11252(S)	18.70	...	...
1048	16742(L)	23.94	...	...
1050	...	...	22912	38.03
1100	17668	24.80	24529	39.54
1150	18613	25.63	...	...
1200	19554	26.43	...	...

Table II presents smooth heat-content and entropy data for the two substances at even 50° intervals in the 400 to 1200°K. range.

The heat-content equations presented below were derived by the method of least squares, using the experimental data from Table I. The average deviations are indicated by the figures in parentheses.

The heat-content equation of the solid RbF was derived to fit conditions:

$$H_T - H_{273.15} = a + bT + cT^2 + dT^{-1} \qquad (1)$$

$$C_p = b + 2cT - \mathrm{d}T^{-2} \text{ where } C_p = 12.04 \text{ at } 283.15\text{°K.}^{5} \qquad (2)$$

$$0 = a + bT + cT^2 + dT^1 \text{ at } 273.15\text{°K.} \qquad (3)$$

The heat-content equation of HfF_4 was made to fit only conditions 1 and 3, since no heat-capacity data were available at low temperatures.

Least square solutions were obtained by means of a Univac-60 electronic computer.[6] Entropy increments were calculated by means of the method suggested by Kelley.[7] The heat-content data are represented by the equations

RbF (solid)

$$H_T - H_{273.15} = -2078 + 7.966T + 4.605 \times 10^{-3}T^2 - 1.206 \times 10^5\ T^{-1} \text{ (273.15 to 1048°K.; } \pm 0.5\%)$$

RbF (liquid)

$$H_T - H_{273.15} = 61518 - 1.1303 \times 10^1 T + 4.416 \times 10^{-4}T^2 - 3.50677 \times 10^7\ T^{-1} \text{ (1048 to 1200°K.; } \pm 0.5\%)$$

HfF_4

$$H_T - H_{273.15} = -11884.9 + 3.1904 \times 10^1\ T + 3.739 \times 10^{-4}T^2 + 8.9889 \times 10^5\ T^{-1} \text{ (273.15 to 1103.3°K.; } \pm 0.7\%)$$

The data show that average deviations of the experimental heat contents from the calculated values are greater at the lower than at the higher temperatures.

(5) J. W. Brønsted, *Z. Elektrochem.*, **20**, 554 (1914).

(6) R. W. Smith, Jr., Supervisory Mathematician, Region V, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Penna.

(7) K. K. Kelley, Bulletin 476, Bureau of Mines, U. S. Department of the Interior, Berkeley, California.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW MEXICO]

Isotopic Exchange between Potassium Iodide and Benzyl Iodides. Solvent Effects[1]

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The rates of exchange between benzyl iodide and potassium iodide and between *p*-nitrobenzyl iodide and potassium iodide, in acetone, are represented by the rate laws: $R = 9.5 \times 10^{10}e^{-13,720/RT}(\mathrm{KI})(\mathrm{BzI})$ and $R = 2 \times 10^{12}e^{-14,350/RT}(\mathrm{KI})(p\text{-}\mathrm{NO_2}\text{-}\mathrm{BzI})$, respectively, where the units of R are mole liter^{-1} sec.$^{-1}$. The rates of exchange, at 0°, between benzyl iodide and potassium iodide in acetone–ethanol, acetone–water, acetone–phenol and acetone–carbon tetrachloride mixtures and between *p*-nitrobenzyl iodide and potassium iodide in acetone–ethanol mixtures have been studied. The inhibitory effect of the hydroxylic compounds has been correlated with their tendency to solvate the iodide ion through hydrogen-bond formation.

Introduction

The isotopic exchange between benzyl iodide and potassium iodide, in methanol and ethanol, was found to proceed *via* an S_N2 mechanism with an easily measurable rate at room temperature.[2] However, under the same conditions, the reaction appeared to be extremely rapid in absolute acetone.(3)

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(1) This paper is a portion of the dissertation presented by J. A. Leary in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1956. Presented before the Physical and Inorganic Division of the American Chemical Society in Atlantic City, September, 1956.

(2) P. Stillson and M. Kahn, THIS JOURNAL, **75**, 3579 (1953).

(3) P. Stillson, Doctoral Thesis, The University of New Mexico, 1951.