

IV, but having *ca.* two-hundred-fold higher tetrathionate concentrations, k_4 increased initially and passed through a maximum as the reaction proceeded, similar to the behavior observed in Experiment 8. The values of k_4 lay within the limits cited above. It is reasonable that in all these experiments with high tetrathionate concentration, where the rate of formation of $S_2O_3OH^-$ is greatly increased, its concentration should tend to build up. Near the start of the experiment, very little of the $S_2O_3OH^-$ reacts with iodine, but as its concentration rises iodine is consumed more rapidly, and the value of k_4 is increased. A suitable choice of the rate law for the disappearance of $S_2O_3OH^-$ would account for the decrease in k_4 toward the end of the reaction.

It was noted in the experiments of Table IV that k_4 increased slightly near the beginning of the experiment. Presumably this is the same effect noted above, but occurring to a much smaller extent because of the lower tetrathionate concentration.

It is evident from the above discussion that the tetrathionate-iodine reaction is indeed complex. If the suggested explanation is correct, two intermediates are building up to appreciable concentrations under certain experimental conditions. Clearly this is not a unique explanation, and considerably more research is needed to test its validity. These results are being reported now because further work could not be carried out at this time.

WASHINGTON, D. C.

RECEIVED FEBRUARY 15, 1951

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids.¹ VIII. Heat Capacity of Zirconium from 14 to 300°K.

BY GORDON B. SKINNER² AND HERRICK L. JOHNSTON

The heat capacities of hafnium-free zirconium have been measured in the temperature range 14 to 300°K., and the derived thermal functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16°K. is 9.29 ± 0.04 e.u.

Introduction

Low temperature heat capacity measurements on zirconium have been made recently by Todd,^{3a} but the purity of his zirconium appears to be questionable. Coughlin and King,^{3b} who used the same specimen as Todd for high temperature heat content measurements, stated that, in addition to 2.15% hafnium, it appeared to contain appreciable amounts of oxygen or nitrogen, or both. The specimen used for the present measurements, having considerably higher purity, should yield more reliable values of the thermal functions of pure zirconium.

Apparatus and Materials

The zirconium used was a special hafnium-free product obtained from the Oak Ridge National Laboratory. It was in the form of small pellets sheared from larger pieces. A careful analysis carried out through the courtesy of the Battelle Memorial Institute, Columbus, Ohio, showed the presence of 0.025 mole % hafnium, 0.67 mole % iron, 0.15 mole % carbon, 0.026 mole % nitrogen, and a total of 0.082 mole % of nineteen other impurities tested for.

In our data a correction was made for the iron present. Vogel and Tonn⁴ found that several per cent. of iron will dissolve in solid zirconium. In making the correction we assumed that the solution is ideal, at least to the extent that the heat capacities are additive. The heat capacities of iron used were those given by Duyckaerts⁵ up to 20°K. and by Kelley in his review bulletin⁶ for higher temperatures. The maximum correction was about 0.3%. No analysis for oxygen could be made on the sample. However, since

the nitrogen content was found to be only 0.026 mole %, it could be expected that the oxygen content would be low also.

The pellets of zirconium were annealed by heating in high vacuum to about 800° for 15 minutes.

"Solid Calorimeter No. 1," of the group of seven vacuum calorimeters described in the first paper⁷ of this series, was used for the heat capacity measurements, and 93.461 g. of pellets (corresponding to 1.0204 moles of zirconium and 0.0069 mole of iron) was placed in it. This amount of zirconium was not sufficient to fill the calorimeter, so that the precision of these measurements is slightly lower than for some others made with the same apparatus.

Experimental Results and Calculations

Experimental heat capacities are summarized in Table I. A comparison with Todd's³ data shows that his values are lower at low temperatures and higher at high temperatures than ours, the curves crossing at about 130°K. This is what would be expected if Todd's zirconium contained oxygen or nitrogen, since the heat capacities of both ZrO_2^8 and ZrN^8 are lower at low temperatures and higher at high temperatures than the heat capacity of zirconium.

Table II gives the heat capacity and derived thermal functions for zirconium at selected integral values of the temperature. The entropy at 298.16°K. is 9.29 e.u., of which, 0.03 e.u. is contributed by the Debye T^3 extrapolation below 14°K. with θ equal to 242. Only two of our experimental heat capacity points above 60°K. deviate from a smooth curve by more than 0.3%. The maximum uncertainty in the entropy (three times the probable error) is 0.04 e.u.

Although our value of the entropy at 298.16°K. agrees well with Todd's,³ which is 9.28 ± 0.08 e.u., our values of the heat content and free energy

(7) H. L. Johnston and E. C. Kerr, *THIS JOURNAL*, **72**, 4733 (1950).

(8) K. K. Kelley, *Ind. Eng. Chem.*, **36**, 377 (1944).

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) Monsanto Chemical Co. Fellow, 1950-1951.

(3) (a) S. S. Todd, *THIS JOURNAL*, **72**, 2914 (1950); (b) J. P. Coughlin and E. G. King, *ibid.*, **72**, 2262 (1950).

(4) R. Vogel and W. Tonn, *Arch. Eisenhüttenw.*, **5**, 387 (1931).

(5) G. Duyckaerts, *Compt. rend.*, **208**, 979 (1939).

(6) K. K. Kelley, U. S. Bureau of Mines, Bulletin No. 477, Contributions to the data of theoretical metallurgy. XI. Entropies of inorganic substances. Revision (1948) of data and methods of calculation.

TABLE I
HEAT CAPACITY OF ZIRCONIUM
Mol. weight 91.22 g., 1.0204 moles

Mean T , °K.	C_p , cal. mole ⁻¹ deg. ⁻¹	Mean T , °K.	C_p , cal. mole ⁻¹ deg. ⁻¹
14.38	0.095	142.59	5.215
16.51	.150	149.94	5.299
18.86	.208	157.56	5.383
20.93	.308	165.96	5.455
23.06	.405	173.99	5.510
25.46	.522	183.07	5.579
27.98	.647	191.77	5.646
31.07	.839	199.90	5.704
34.07	1.050	208.14	5.739
37.55	1.321	215.00	5.784
41.43	1.611	221.10	5.813
44.97	1.860	227.40	5.832
48.52	2.108	234.19	5.836
53.59	2.435	239.89	5.894
58.91	2.799	245.00	5.869
64.62	3.122	250.43	5.912
70.33	3.400	255.74	5.929
76.04	3.647	261.35	5.963
82.86	3.920	265.96	5.967
89.22	4.129	270.30	5.989
95.48	4.328	274.16	5.995
101.97	4.512	278.18	5.988
108.61	4.680	282.00	5.974
115.03	4.814	286.07	5.991
122.09	4.943	290.11	6.000
128.70	5.035	293.81	6.006
135.50	5.122	298.23	6.004

TABLE II
THERMAL FUNCTIONS OF ZIRCONIUM

T , °K.	C_p^0 , cal. mole ⁻¹ deg. ⁻¹	S^0 , cal. mole ⁻¹ deg. ⁻¹	$H^0 - H_0^0$, cal. mole ⁻¹	$(H^0 - H_0^0)/T$, cal. mole ⁻¹ deg. ⁻¹	$-(H^0 - H_0^0)/T^2$, cal. mole ⁻¹ deg. ⁻²
14 ^a	0.090	0.030	0.31	0.022	0.008
25	0.489	0.169	3.16	.126	.043
50	2.212	1.016	36.0	.720	.296
75	3.609	2.200	110.2	1.469	.730
100	4.460	3.362	211.7	2.117	1.245
125	4.986	4.421	330.5	2.644	1.776
150	5.299	5.359	459.3	3.062	2.297
175	5.525	6.193	594.8	3.399	2.795
200	5.691	6.942	735.1	3.675	3.267
225	5.824	7.621	879.1	3.907	3.714
250	5.918	8.240	1025.6	4.103	4.137
275	5.981	8.807	1174.5	4.271	4.536
298.16	6.012	9.292	1313.3	4.405	4.887
300	6.014	9.329	1324.4	4.415	4.914

^a Debye T^3 extrapolation below 14°K. with θ equal to 242.

function are lower than those calculated from his data.

Acknowledgments.—We wish to acknowledge the assistance of the United States Atomic Energy Commission in making available to us the hafnium-free zirconium used in this research.

We particularly wish to acknowledge the assistance of Mr. Nathan C. Hallet, who gave assistance in the assembly and calibration of the calorimeter, and with the measurements.

COLUMBUS 10, OHIO

RECEIVED FEBRUARY 20, 1951

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. IX. Heat Capacity and Thermodynamic Properties of Cuprous Oxide from 14 to 300°K.¹

BY JIH-HENG HU AND HERRICK L. JOHNSTON

The heat capacities of cuprous oxide have been measured in the temperature range 14 to 300°K., and the derived thermodynamic functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16°K. comes out 22.44 ± 0.07 e.u. Our data gave no evidence of a transition between 14 and 303°K.

Introduction

Pitzer and Smith^{2a} and Johnston and Weaver^{2b} found evidence for a second order transition in silver oxide in the neighborhood of 35°K. Since there was some reason to suspect that this transition might be associated with cooperative phenomena in the cuprite type of lattice that characterized Ag₂O it was thought desirable to measure the heat capacity of cuprite at low temperatures. The only previous measurements on Cu₂O at low temperatures were those of Millar³ who covered the temperature range 75–291°K.

Apparatus and Materials

The cuprous oxide used was obtained by precipitating a warm Fehling solution with dextrose. Af-

ter it had been washed with CO₂-free water, alcohol and ether, it was dried over calcium chloride in a vacuum desiccator. Its copper content was determined by electrolytic analysis. On the assumption that this entire copper content was derived from cuprous oxide, the sample contained 99.80% cuprous oxide. An X-ray diffraction pattern showed lattice constants characteristic of the cuprite lattice.

"Solid calorimeter No. 6" of the group of seven vacuum calorimeters described in the first paper⁴ of this series was filled with 112.282 g. (0.7844 mole) of cuprous oxide for heat capacity measurements.

Experimental Results

Experimental heat capacities are summarized in Table I. A large scale plot of our data gives no evidence of a transition between 14 and 303°K. Table II gives the heat capacity and derived thermodynamic functions for cuprous oxide at selected

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation. Paper VIII, THIS JOURNAL, **73**, 4549 (1951).

(2) (a) K. S. Pitzer and W. V. Smith, *ibid.*, **59**, 2633 (1937); (b) H. L. Johnston and C. E. Weaver, unpublished results.

(3) R. W. Millar, *ibid.*, **51**, 215 (1929).

(4) H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 4733 (1950).