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.$^{-1}$	$-(F^0 - H_0^0)/T$, cal. mole^{-1} deg.$^{-1}$
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 coöperative phenomena in the cuprite type of lattice that characterized Ag_2O it was thought desirable to measure the heat capacity of cuprite at low temperatures. The only previous measurements on Cu_2O at low temperatures were those of Millar[3] 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. After it had been washed with CO_2-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 paper[4] 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

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[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).

integral values of the temperature. The entropy at 298.16°K. is 22.44 e.u., of which 0.41 e.u. is contributed by extrapolation below 16°K. Millar[3] reported a value of 21.7 ± 1.0 e.u., based on his own data from 75 to 291°K. and an extrapolation below 75°K.[5]

TABLE I

MOLAR HEAT CAPACITY OF CUPROUS OXIDE

Mol. wt. 143.14 g., 0.7844 mole

Mean T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$	Mean T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$
14.72	0.697	88.31	8.952
16.47	0.864	94.28	9.254
18.99	1.156	101.73	9.575
21.31	1.472	109.75	9.856
23.49	1.793	116.62	10.12
25.22	2.073	124.00	10.39
26.00	2.190	131.66	10.70
28.22	2.567	138.81	10.97
28.75	2.642	145.42	11.21
30.53	2.960	153.63	11.48
31.31	3.087	160.73	11.73
32.84	3.359	166.88	11.92
35.70	3.879	174.06	12.15
38.89	4.419	181.20	12.37
40.87	4.695	187.89	12.57
42.72	5.007	194.89	12.78
43.39	5.072	203.79	12.99
46.69	5.527	212.62	13.26
47.04	5.602	220.84	13.47
50.34	5.961	229.00	13.71
51.84	6.187	236.16	13.87
54.00	6.410	243.54	14.03
57.01	6.751	252.12	14.22
57.82	6.813	259.67	14.43
60.65	7.133	269.67	14.65
61.65	7.176	275.47	14.78
64.01	7.404	283.67	14.95
69.44	7.830	291.67	15.09
76.39	8.304	299.64	15.22
82.80	8.663		

TABLE II

THERMODYNAMIC FUNCTIONS FOR CUPROUS OXIDE

T, °K.	C_p 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.$^{-1}$	$-(F^0 - H_0^0)/T$ cal. mole^{-1} deg.$^{-1}$
16	0.807	0.4065	4.398	0.2749	0.1316
25	2.022	1.0014	16.803	0.6721	0.3293
50	5.966	3.6809	119.28	2.3856	1.2953
75	8.205	6.5718	299.42	3.9923	2.5795
100	9.485	9.1226	521.84	5.2184	3.9042
125	10.452	11.345	771.30	6.1704	5.175
150	11.360	13.332	1044.0	6.9600	6.372
175	12.180	15.146	1338.5	7.6486	7.497
200	12.917	16.821	1652.3	8.2615	8.560
225	13.584	18.381	1983.7	8.8164	9.565
250	14.197	19.845	2331.1	9.3244	10.521
275	14.756	21.225	2693.1	9.7931	11.432
298.16	15.210	22.436	3040.3	10.197	12.239
300	15.242	22.530	3068.3	10.228	12.302

Our estimate of the uncertainty in the entropy is ±0.07 e.u., of which ±0.04 e.u. is due to the uncertainty in the extrapolated portion below 16°K.

Acknowledgments.—We wish to acknowledge the assistance of Mr. Nathan C. Hallett in checking the experimental work and in giving assistance with some of the measurements. We are also indebted to Mr. Gordon B. Skinner for making the X-ray analyses.

[5] Millar's cuprous oxide was prepared by heating pure cupric oxide under reduced pressure at 1000°.

COLUMBUS 10, OHIO RECEIVED FEBRUARY 20, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Adsorption of Water by Carbon[1]

BY CONWAY PIERCE, R. NELSON SMITH, J. W. WILEY AND H. CORDES

Water isotherms are given for porous and non-porous carbons. A non-porous carbon adsorbs little water, as compared with other vapors, but activated charcoals hold nearly the same liquid volume of water as of other vapors. The net heat appears to be zero for the initial adsorption of water, then as more molecules are adsorbed the net heat becomes positive. This effect is ascribed to the contribution of lateral interactions with previously adsorbed molecules. At elevated temperatures the initial net heat of adsorption appears to have a large negative value, but it is shown that this effect may be due to a reaction of carbon with water which may occur slowly even at room temperature. Hydrogen and carbon dioxide are produced in the reaction and some of the oxygen is held as a surface complex, which increases the surface affinity for water. An upturn in a water isotherm below $0.95p_0$ appears to be associated with the presence of capillaries. Water isotherms are used to detect capillaries in certain carbon blacks.

During the past thirty years many isotherms have been reported for adsorption of water vapor by activated charcoal, but comparatively little work has been done with non-porous carbon. The isotherms of charcoals show a variety of forms and there is little correlation of the charcoal data with those for non-porous surfaces. The work herein reported has been done with samples of both porous and non-porous carbons for which the isotherms for other adsorbates are known, with the hope of gaining a better understanding of the factors which make water adsorption unlike that of other vapors.

Water adsorption studies prior to 1946 have been reviewed by Emmett.[2] The most extensive work since this review is that done by Wiig and Juhola,[3a,b] and by Harkins, Jura and associates.[3c,d]

[1] This is a progress report of work done under Contract N8 onr 54700 with the Office of Naval Research.

[2] P. H. Emmett, *Chem. Revs.*, **43**, 69 (1948).

[3] (a) E. O. Wiig and A. J. Juhola, THIS JOURNAL, **71**, 561 (1949); (b) A. J. Juhola and E. O. Wiig, *ibid.*, **71**, 2069, 2078 (1949); (c) W. D. Harkins, G. Jura and E. H. Loeser, *ibid.*, **68**, 554 (1946); (d) P. R. Basford, G. Jura and W. D. Harkins, *ibid.*, **70**, 1444 (1948).