[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES]

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Sodium Superoxide, Potassium Superoxide and Sodium Peroxide

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Heat capacity measurements of sodium superoxide, potassium superoxide and sodium peroxide were conducted throughout the temperature range from 50 to 298°K. Two heat capacity maxima were found for each of the superoxides. No anomalous behavior was observed for sodium peroxide. The entropies were evaluated in cal./deg. mole at 298.16°K. as 27.7 ± 0.3 for sodium superoxide, 27.9 ± 0.6 for potassium superoxide and 22.6 ± 0.3 for sodium peroxide.

Interest in the superoxides of sodium and potassium resides in their use as solid-state storage media for oxygen. One-half of the contained oxygen is liberated merely by contact with water and thus is readily available for any desired purpose. Thermodynamic calculations pertaining to the methods of manufacture of these substances have been hampered by lack of requisite basic data. The present paper supplies low temperature heat capacity and entropy values for these superoxides and also for sodium peroxide. No similar data for any of these substances have been reported previously.

Materials.—The materials were furnished by J. L. Margrave, Chemistry Department, University of California, who had obtained them for thermochemical measurements from the Mine Safety Appliance Co. through the courtesy of C. B. Jackson and W. H. Schechter. Mr. Margrave also supplied the results of chemical analyses, X-ray diffractions and other tests necessary for evaluating the purities. Although the impurity contents may appear rather high, the difficulties in preparing these substances in pure form should be recognized. The samples furnished are of about as good quality as it is reasonably possible to obtain, and most of the impurities are of a nature to permit adequate correction for their influence upon the heat capacity measurements.

The sodium superoxide was analyzed for sodium and available oxygen; in addition, a quantitative water solution of the material was analyzed for total basicity and for carbonate. The results indicate the sample to be 92.5% sodium superoxide, 6.0% sodium peroxide and 1.5% sodium carbonate.

The potassium superoxide was analyzed for potassium, sodium and available oxygen. Total basicity and carbonate content of a quantitative water solution were determined. The results conform with the assignment of 92.4% potassium superoxide, 3.5% sodium peroxide and 4.1% potassium carbonate. The X-ray diffraction pattern contained strong, clear lines of potassium superoxide. Only two weak impurity (unidentified) lines appeared.

The sodium peroxide was analyzed for sodium and available oxygen, and total basicity and carbonate contents of a quantitative solution were measured. The results indicate 94.0% sodium peroxide, 3.6% sodium oxide and 2.4% sodium carbonate. The X-ray diffraction pattern contained only lines of sodium peroxide.

The samples were transferred in a dry-box from the original sealed containers to the filling tube for the calorimeter. The filling tube was then attached to the calorimeter by a short piece of rubber tubing and the calorimeter was filled without exposure of the sample. The following sample masses were employed in the measurements: 122.50 g. of sodium superoxide, 85.05 g. of potassium superoxide and 131.20 g. of sodium peroxide.

Measurements.—The heat capacity measurements were conducted with previously described[1] apparatus and methods.

Corrections in the reported results have been made for the sodium peroxide and sodium carbonate contents of the sodium superoxide sample, for the sodium peroxide and potassium carbonate (assuming the same molal heat capacity as for sodium carbonate) contents of the potassium superoxide sample, and for the sodium carbonate content of the sodium peroxide sample. No satisfactory means was available for correcting for the sodium oxide content of the sodium peroxide sample, but estimates indicated that this correction probably would be small.

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T. °K.	C_p, cal./deg. mole
		NaO_2 (mol. wt. 54.997)			
52.13	4.688	165.83	16.26	219.11	30.51(b)
56.02	5.209	175.79	17.04	221.79	73.74(b)
60.41	5.866	185.70	18.71	223.27	103.50(b)
64.97	6.579	187.15	19.47(a)	224.55	61.74
69.61	7.274	191.51	28.97(a)	225.02	47.85(b)
74.36	7.929	194.23	60.78	227.98	26.73(b)
79.71	8.594	194.38	62.32(a)	232.14	17.51(b)
83.56	9.017	196.23	72.40(a)	235.94	17.37
94.46	10.29	198.49	39.95(a)	245.75	17.26
104.34	11.31	201.82	26.39(a)	255.89	17.20
114.45	12.30	206.02	19.13	266.19	17.21
126.97	13.36	206.03	19.02(a)	276.01	17.20
135.91	14.07	210.30	19.71(b)	286.26	17.23
145.86	14.82	214.99	21.71(b)	296.46	17.23
155.74	15.49	215.87	22.45	(298.16)	17.24
		KO_2 (mol. wt. 71.096)			
52.59	6.436	156.04	16.35	224.64	18.35(d)
57.29	7.153	166.36	16.88	226.25	18.52
62.05	7.932	176.21	17.39	228.96	18.85(d)
66.72	8.663	183.54	17.95(c)	232.87	18.72(d)
71.49	9.325	186.22	18.25	236.37	18.13
76.19	9.939	188.63	18.82(c)	236.93	18.04(d)
80.00	10.40	192.51	31.81(c)	241.47	17.62(d)
84.07	10.90	195.31	28.98	246.14	17.60
94.83	12.05	195.86	22.79(c)	256.71	17.73
104.70	12.94	200.25	17.31(c)	266.24	17.90
114.88	13.79	205.02	17.17(c)	276.41	18.11
125.06	14.54	206.44	17.25	286.62	18.31
136.09	15.25	216.68	17.73	296.72	18.50
146.17	15.85	219.56	17.93(d)	(298.16)	18.53
		Na_2O_2 (mol. wt. 77.994)			
52.31	2.850	114.49	11.51	215.99	18.76
56.81	3.443	123.72	12.53	225.87	19.17
61.35	4.116	137.21	13.85	235.68	19.51
65.80	4.807	145.08	14.54	244.94	19.75
70.33	5.490	154.62	15.29	255.27	20.17
74.93	6.175	164.79	16.02	265.47	20.48
80.22	6.968	175.81	16.76	275.32	20.76
84.44	7.590	184.78	17.25	285.55	21.06
95.78	9.180	195.21	17.79	296.22	21.26
106.35	10.52	205.61	18.28	(298.16)	(21.35)

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[1] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bureau of Mines Tech. Paper 686 (1946).

The results, expressed in defined cal./deg. mole (1 cal. = 4.1840 abs. joules), are listed in Table I and plotted in Fig. 1. Molal weights accord with the 1951 International Atomic Weights.[2]

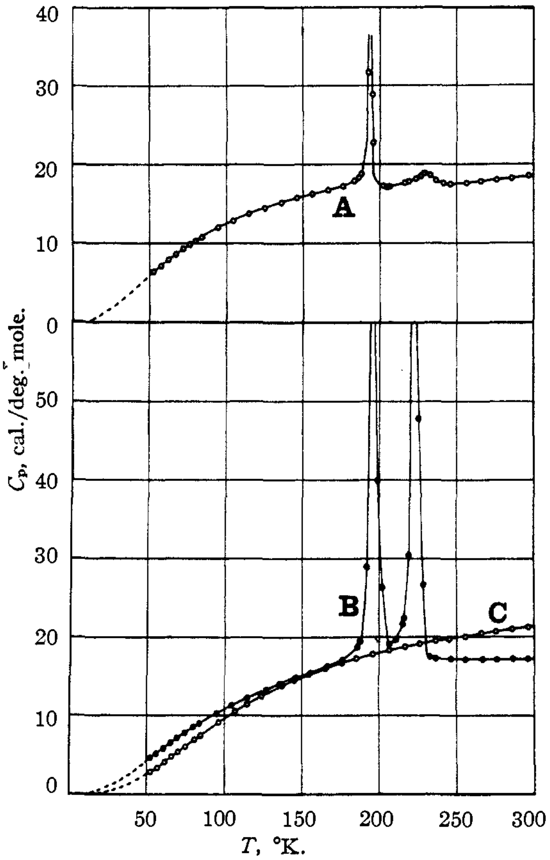

Fig. 1.—Heat capacities: A, KO_2; B (filled circles), NaO_2; C (open circles), Na_2O_2.

The heat capacity of sodium superoxide passes through two high peaks at 196.5 and 223.3°K. The highest heat capacities actually measured in these peak regions are 27.40 cal./deg. mole at 196.23°K. and 103.50 cal./deg. mole at 223.27°K. These values are, respectively, more than 3.5 and 5 times the "normal" values in the surrounding region. The two series of determinations labeled (a) and (b) in Table I were made without temperature gaps and with smaller than usual temperature intervals, to establish the shape of the peaks. In addition to the results in Table I, two total heat absorption measurements were made for the interval 185.00–208.00°K., the results being 745.4 and 746.3 cal./mole. Likewise, two total heat absorption measurements for the interval 208.00–235.00°K. gave 838.8 and 838.6 cal./mole. The existence of these two transformations in sodium superoxide also has been established by X-ray diffraction studies.[3]

The heat capacity of potassium superoxide also shows two peaks. The lower temperature peak, at 193.5°K., is quite large, the maximum heat capacity actually measured being 31.81 cal./deg. mole at 192.51°K., which is about 50% greater than the "normal" values in the surrounding region. It is interesting to note that Neuman[4] has reported a marked color change at 197.7°K. The upper temperature peak, at 230.9°K., is small as is evident in Fig. 1. The values labeled (c) and (d) in Table I were obtained in continuous series without temperature gaps and with smaller than usual temperature intervals, to trace the course of the curves in the peak regions. The total heat absorption between 180.00 and 208.00°K. was determined in two separate measurements as 553.6 and 552.0 cal./mole. One measurement was made of the total heat absorption for the interval 217.00–243.00°K., the result being 478.0 cal./mole.

The heat capacity values for sodium peroxide appear normal in all respects, and no unusual behavior was observed during the measurements.

Entropies at 298.16°K.

The measured portion of the entropy of sodium superoxide was obtained by Simpson rule integration of C_p *vs.* log T plots for the intervals 51.00–185.00°K. and 235.00–298.16°K. and by separate treatment of the two anomalous intervals, 185.00–208.00°K. and 208.00–235.00°K. To obtain the entropy increments for these anomalous intervals, the total heat absorptions were divided by the effective mean temperatures derived from careful consideration of the two series of consecutive heat capacity measurements labeled (a) and (b) in Table I. The process for determining this effective mean temperature was to evaluate the sums $A = \Sigma C_p \mathrm{d}T$ and $B = \Sigma\ C_p \mathrm{d}T/T$ from the heat capacity measurements for each interval. The ratio B/A then gives the mean effective temperature to be applied to the total heat measurements. The mean effective temperatures so calculated for these intervals are 196.2 and 221.7°K., yielding the entropy increments 745.85/196.2 = 3.801 and 838.7/221.7 = 3.783 cal./deg. mole.

The measured portion of the entropy of potassium superoxide was obtained similarly. Simpson rule integrations of C_p *vs.* log T plots were made for the intervals 51.00–180.00°K., 208.00–217.00°K., and 243.00–298.16°K. The entropies for the anomalous intervals 180.00–208.00°K. and 217.00–243.00°K. were obtained as described for sodium superoxide, the mean effective temperatures being 193.5 and 229.7°K.

In the case of sodium peroxide, calculation of the measured portion of the entropy involved only Simpson rule integration of the C_p *vs.* log T plot between 51.00 and 298.16°K.

The extrapolated portions of the entropies, below 51.00°K., were obtained by use of Debye and Einstein functions. The following empirical function sums fit the experimental data to within the maximum deviation and for the temperature range shown in parentheses

NaO_2: $D(175/T) + 2E(313/T)$(1.4%, 51–95°K.)
KO_2: $D(139/T) + 2E(260/T)$(1.1%, 51–100°K.)
Na_2O_2: $D(252/T) + 3E(399/T)$(3.4%, 51–298°K.)

These function sums yield the extrapolated portions of the entropies listed in Table II. It is seen that these extrapolated portions are only 8.1, 12.2 and 4.7% of the totals for 298.16°K.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

Substance	NaO_2	KO_2	Na_2O_2
0–51.00°K. (extrap.)	2.23	3.39	1.06
51.00–298.16°K. (meas.)	25.47	24.49	21.59
$S°_{298.16}$	27.7 ± 0.3	27.9 ± 0.6	22.6 ± 0.3

The entropy value of sodium peroxide is about the

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[2] E. Wichers, THIS JOURNAL, 74, 2447 (1952).

[3] G. F. Carter, Ph.D. Thesis, Chemistry Department, University of California, 1952.

[4] E. W. Neuman, *J. Chem. Phys.*, 29, 3583 (1935).

magnitude that would have been expected beforehand. The other two values, especially that for sodium superoxide, are considerably larger than would have been predicted, which is partly attributable to the heat capacity maxima.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, BUREAU OF MINES]

High Temperature Heat Contents of Hafnium Dioxide and Hafnium Tetrachloride

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High temperature heat contents of hafnium dioxide and hafnium tetrachloride were measured from 298.16°K. to 1804 and 486°K., respectively. A table of smooth heat content and entropy increment data above 298.16°K. was compiled, and heat content equations representing the data were derived.

Introduction

Recent progress in the large-scale separation and purification of zirconium and hafnium has led to the availability of hafnium and some of its compounds of sufficient purity and in adequate amounts for measuring thermodynamic properties. The present paper reports heat content measurements covering the range from 298.16°K. to 1804°K. for hafnium dioxide, and from 298.16°K. to 486°K. for hafnium tetrachloride. No high temperature heat content data have been reported previously for either substance.

Materials

The hafnium dioxide and hafnium tetrachloride were furnished by the Northwest Electrodevelopment Laboratory of the Bureau of Mines at Albany, Oregon, along with the results of chemical and spectrographic analyses.

The zirconium content of the dioxide is 1.45% of the total hafnium plus zirconium content. Other impurities amount to about 0.37%, being principally 0.21% iron, 0.08% silicon, 0.05% titanium, and about 0.005% each of lead, magnesium, zinc and nickel. An X-ray diffraction by R. E. Lorenson of this Laboratory showed the structure to be similar to that of the monoclinic variety of zirconium dioxide. In correcting the heat content measurements, the sample was considered as composed of 98.34% hafnium dioxide and 1.66% zirconium dioxide, in accordance with the above-designated zirconium content.

The zirconium content of the hafnium tetrachloride is 2.35% of the total hafnium plus zirconium content. Other impurities amount to about 0.08%, principally 0.03% iron, 0.01% silicon, 0.01% titanium, and about 0.005% each of zinc and nickel. Analysis for chlorine was made by K. R. Bonnickson of this Laboratory. The determined amount is 44.55%, as compared with the calculated 44.81% (allowance being made for the zirconium content). In correcting the heat content measurements, the sample was considered as composed of 96.69% hafnium tetrachloride and 3.31% zirconium tetrachloride.

Measurements and Results

The "dropping" method was used for the measurements, using apparatus and experimental procedures described previously.[1,2] The calorimeter was calibrated electrically, and during the course of the measurements the furnace thermocouple was calibrated frequently at the melting point of pure gold.

The samples were contained in platinum–rhodium alloy capsules, the heat contents of which were determined by separate experiments. The capsule containing the hafnium tetrachloride was sealed gas-tight by pinching the neck shut and soldering it with gold, after first evacuating of air and filling the pore space with helium. A correction was made for the heat content of the small amount of gold used. The neck of the capsule containing the hafnium dioxide was merely pinched shut.

The measured heat content data, expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole, are listed in Table I. Molal weights are computed according to the 1951 International Atomic Weights.[3]

TABLE I

MEASURED HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
		HfO_2 (mol. wt. 210.60)			
382.7	1250	814.1	8,830	1283.9	17,880
388.6	1330	862.5	9,700	1383.4	19,870
481.5	2870	894.3	10,390	1488.6	21,980
593.7	4785	986.5	12,110	1591.2	24,080
673.3	6255	1088.0	14,050	1698.3	26,250
794.4	8460	1192.5	16,070	1803.6	28,470
		$HfCl_4$ (mol. wt. 320.43)			
358.3	1750	426.5	3,800	459.8	4,810
393.1	2820	449.0	4,460	485.7	5,580
406.8	3230				

Corrections for the corresponding zirconium compounds contained by the two substances were made, using the data of Coughlin and King.[4]

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPY VALUES (CAL./DEG. MOLE) ABOVE 298.16°K.

	HfO_2		$HfCl_4$	
T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
350	....	...	1520	4.69
400	1,540	4.43	3010	8.68
450	....	...	4510	12.21
500	3,170	8.06	6020	15.39
600	4,900	11.22		
700	6,710	14.01		
800	8,570	16.49		
900	10,450	18.71		
1000	12,350	20.71		
1100	14,280	22.55		
1200	16,230	24.24		
1300	18,200	25.82		
1400	20,200	27.30		
1500	22,220	28.69		
1600	24,260	30.01		
1700	26,320	31.26		
1800	28,400	32.45		

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(1) J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, Bureau Mines Tech. Paper 686 (1946).

(3) E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

(4) J. P. Coughlin and E. G. King, *ibid.*, **72**, 2262 (1950).