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Low Temperature Heat Capacities and Entropies at 298.15°K. of Some Oxides of Gallium, Germanium, Molybdenum and Niobium

BY E. G. KING

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Heat capacities of β-gallium oxide, germanium dioxide (soluble form), molybdenum dioxide and niobium dioxide were measured in the temperature range 51 to 298°K. All four substances gave normal heat capacity–temperature curves. The entropies at 298.15°K. are, respectively, 20.31 ± 0.10, 13.21 ± 0.10, 11.06 ± 0.05 and 13.03 ± 0.07 cal./deg. mole.

No previous low temperature heat-capacity data have been reported for the dioxides of germanium, molybdenum and niobium, and no reliable entropy values for these substances have been available. Adams and Johnston[1] have published data for β-gallium oxide that are in substantial agreement with the present work, taking account of the difference in purity of the investigated samples.

Materials.—The β-gallium oxide was loaned for this work by C. E. Holley, Jr., of the Los Alamos Scientific Laboratory. As received, the sample contained 0.4% water, which was removed by heating for 5 hr. in platinum at 1300°. This treatment also rendered the sample non-hygroscopic. Spectrographic analysis, provided by Holley, showed the presence of 0.05% of zinc oxide. This was the major impurity; all other contaminants were in amounts less than 0.01%. It appears safe to conclude that purity of the substance was 99.9%. Powder X-ray diffraction examination agreed with the patterns reported by Laubengayer and Engle[2] and Foster and Stumpf.[3]

Germanium dioxide (soluble form), with a claimed purity of 99.99%, was obtained from Varlacoid Chemical Co. Spectrographic analysis, by G. M. Gordon of the Division of Mineral Technology of the University of California, indicated at least 99.95% purity, with no contaminant present in amount greater than 0.01%. The X-ray diffraction pattern agreed with that of Swanson and Tatge.[4]

Molybdenum dioxide was prepared by heating reagent grade trioxide in hydrogen for a total of 19 days at 390–410°. Analyses by hydrogen reduction at 900° gave 74.99% molybdenum, which is the theoretical value. The X-ray diffraction pattern agreed with the ASTM catalog.

Niobium dioxide was prepared by reducing high-purity niobium pentoxide with hydrogen at 950–1000°. Eight batches were reduced for 4 hr. each, combined and reduced for another 4 hr. Completion of conversion to dioxide was tested by heating a portion of the product to 1450° in hydrogen; no weight change was observed. Analysis, made by reconverting to pentoxide, indicated that the substance was 99.9% niobium dioxide. Analysis by dissolving, precipitating the niobium as hydroxide and igniting to constant weight showed the substance to be virtually 100% pure, in agreement with the first method. The X-ray diffraction pattern checked that given by Brauer.[5]

Measurements and Results.—The apparatus used is the same as previously described.[6] The experimental heat-capacity values appear in Table I, expressed in defined calories per deg. mole (1 cal. = 4.1840 abs. joules). Molecular weights were obtained from the 1954–55 Report on Atomic Weights.[7]

The behavior of the four substances was regular throughout the measured temperature range, and the heat capacity–temperature curves appear entirely normal.

TABLE I

HEAT CAPACITIES (CAL./DEG. MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
$Ga_2O_3(\beta)$ (mol. wt., 187.44)					
53.81	2.786	114.63	9.402	216.26	17.83
58.36	3.274	124.55	10.41	226.28	18.47
62.79	3.752	135.99	11.52	236.27	19.04
67.37	4.257	145.48	12.42	246.10	19.57
71.99	4.775	155.76	13.33	256.50	20.16
76.45	5.261	165.77	14.17	266.30	20.62
80.29	5.711	175.70	14.98	276.63	21.10
84.16	6.122	186.26	15.79	286.83	21.53
94.92	7.306	196.26	16.50	296.34	21.98
105.09	8.414	206.43	17.21	298.15	(22.02)
GeO_2 (mol. wt., 104.60)					
53.97	2.524	114.50	6.175	216.39	10.29
58.36	2.805	124.61	6.690	226.11	10.60
62.88	3.106	136.30	7.248	236.21	10.88
67.42	3.410	145.73	7.686	245.77	11.14
72.13	3.716	155.95	8.115	256.32	11.45
76.51	3.986	166.05	8.522	266.51	11.70
81.73	4.316	176.03	8.905	276.41	11.95
86.03	4.571	186.14	9.275	286.79	12.19
94.90	5.096	196.08	9.607	296.24	12.43
104.91	5.670	206.48	9.974	298.15	(12.45)
MoO_2 (mol. wt., 127.95)					
53.31	1.007	114.84	4.875	215.51	10.58
57.41	1.221	125.00	5.564	226.01	11.02
61.61	1.440	135.77	6.277	236.26	11.41
66.05	1.690	145.61	6.913	245.67	11.73
70.92	1.985	155.99	7.546	256.32	12.10
75.82	2.275	165.87	8.128	266.21	12.44
82.14	2.682	175.90	8.669	276.10	12.74
86.86	2.979	186.08	9.214	286.48	13.05
94.94	3.527	196.06	9.685	296.00	13.34
104.96	4.211	206.29	10.17	298.15	(13.38)
NbO_2 (mol. wt., 124.91)					
53.45	1.733	114.69	6.066	216.49	11.37
58.11	2.026	124.96	6.763	226.25	11.75
62.58	2.341	136.02	7.452	236.23	12.05
67.17	2.667	145.71	8.054	245.71	12.37
71.77	3.004	156.03	8.635	256.53	12.70
76.56	3.342	165.95	9.156	266.33	12.97
81.56	3.718	176.26	9.662	276.19	13.23
86.26	4.058	185.96	10.14	286.82	13.47
95.12	4.700	196.07	10.57	296.30	13.74
104.85	5.396	206.31	10.99	298.15	(13.74)

Adams and Johnston's[1] values for β-gallium oxide are lower than those reported here, the amount

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[1] G. B. Adams, Jr., and H. L. Johnston, THIS JOURNAL, **74**, 4788 (1952).

[2] A. W. Laubengayer and N. R. Engle, *ibid.*, **61**, 1210 (1939).

[3] L. M. Foster and H. C. Stumpf, *ibid.*, **73**, 1590 (1951).

[4] H. E. Swanson and E. Tatge, "Natl. Bur. Standards Circular 531," vol. I, June 15, 1953.

[5] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

[6] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1941).

[7] E. Wichers, THIS JOURNAL, **78**, 3235 (1956).

ranging from 0.6% at 50°K. to a maximum of 1.3% at 225°K. and then decreasing to 0.3% at 298°K. Their sample contained over 1% of impurities, which may explain part of the difference. The agreement, however, may be considered as substantial from the viewpoint of the calculation of the entropy at 298.15°K.[8]

Entropies at 298.15°K.—The entropy increments for the measured temperature range (51–298°K.) were obtained by Simpson-rule integrations of plots of C_p against log T. The increments below 51°K. were obtained by extrapolation, using the following empirical combinations of Debye and Einstein functions which fit the measured heat capacities from 51 to 298°K. to within the maximum amounts shown.

$Ga_2O_3(\beta)$: $D(286/T) + E(293/T) + 3E(730/T)$ (1.5%)
GeO_2: $D(246/T) + E(531/T) + E(1083/T)$ (1.9%)
MoO_2: $D(399/T) + E(538/T) + E(836/T)$ (1.6%)
NbO_2: $D(309/T) + E(503/T) + E(790/T)$ (1.1%)

The results of the entropy calculations appear in Table II.

TABLE II

ENTROPIES AT 298.15°K. (CAL./DEG. MOLE)

Substance	$S°_{51} - S°_0$ (extrap.)	$S°_{298.15} - S°_{51}$ (meas.)	$S°_{298.15}$
$Ga_2O_3(\beta)$	0.87	19.44	20.31 ± 0.10
GeO_2 (soluble)	1.06	12.15	13.21 ± .10
MoO_2	0.31	10.75	11.06 ± .05
NbO_2	0.62	12.41	13.03 ± .07

The present entropy value for β-gallium oxide at 298.15°K. is 0.1 unit higher than that reported by Adams and Johnston.[1] The agreement is within the limits of error set by each of the investigations.

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[8] For definition of 25.00° as 298.15°K. see *Comité intern. poids et measures, procès-verbaux de séances de 1954*, **24**, T79 (1955).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Contents above 298.15°K. of Oxides of Cobalt and Nickel

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High temperature heat content measurements of cobaltous oxide, cobalt spinel and nickelous oxide were conducted from 298°K. to 1803, 999 and 1810°K., respectively. The heat content–temperature curve of nickelous oxide shows abrupt changes in slope at 525 and 565°K., indicating second-order transformations. A table of heat content and entropy increments above 298.15°K. and heat content equations are included for use in thermodynamic calculations.

The literature contains no previous high temperature heat-content data for cobaltous oxide (CoO) or cobalt spinel (Co_3O_4). Kapustinsky and Novosel'tsev[1] (to 1395°K.) and Tomlinson and co-workers[2] (to 1108°K.) have measured nickelous oxide (NiO). The present paper reports results to 1803°K. for cobaltous oxide, to 999°K. for cobalt spinel and to 1810°K. for nickelous oxide. Low temperature heat capacity measurements and entropy evaluations at 298.15°K. for these substances were published by King.[3]

Materials.—The cobaltous oxide was a portion of the sample used by King[3] in low temperature heat capacity measurements. Before use in the present work it was reheated for 72 hr. in air at 1180–1230°, then 28 hr. in helium at 1150–1160° and reanalyzed. The analysis gave 78.61% cobalt, 21.36% oxygen, 0.02% silica and 0.01% sulfur, as compared with the theoretical 78.65% cobalt and 21.35% oxygen.

The cobalt spinel and nickelous oxide also were portions of the samples described by King[3] and were used without additional treatment.

Measurements and Results.—Previously described apparatus[4] was used in the heat content measurements. The substances were enclosed in platinum–rhodium capsules from which the air was pumped and replaced by helium before sealing the necks by platinum welding. The heat contents of the empty capsules were determined in separate experiments. The furnace thermocouple was checked frequently against the melting point of pure gold.

TABLE I

MEASURED HEAT CONTENTS ABOVE 298.15°K.[6] (CAL./MOLE)

T, °K.	$H_T - H_{298.15}$	T, °K.	$H_T - H_{298.15}$	T, °K.	$H_T - H_{298.15}$
		CoO (mol. wt., 74.94)			
402.5	1,325	900.8	7,790	1398.5	14,660
501.1	2,575	1011.1	9,260	1497.9	16,060
602.8	3,900	1100.8	10,490	1599.8	17,590
701.5	5,195	1201.5	11,850	1702.7	19,180
801.6	6,495	1303.8	13,280	1803.2	20,770
		Co_3O_4 (mol. wt., 240.82)			
386.8	2,820	807.7	19,120	984.7	27,650
497.9	6,750	896.1	23,110	991.2	27,970
599.4	10,600	950.7	25,750	998.1	28,240
706.6	14,900	975.0	27,100	999.1	28,460
751.3	16,820	....	....	....	....
		NiO (mol. wt., 74.71)			
364.9	750	556.2	3,345	1206.9	11,750
433.0	1,580	561.2	3,445	1224.4	12,020
502.9	2,585	572.3	3,585	1304.3	13,120
513.2	2,740	672.3	4,865	1406.3	14,540
524.2	2,925	785.7	6,315	1500.9	15,840
535.5	3,080	873.3	7,440	1604.4	17,360
544.6	3,205	964.9	8,620	1709.8	18,890
554.2	3,335	1088.8	10,210	1809.7	20,440

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[1] A. F. Kapustinsky and K. A. Novosel'tsev, *J. Phys. Chem. (U. S. S. R.)*, **11**, 61 (1938).

[2] J. R. Tomlinson, L. Domash, R. G. Hay and C. W. Montgomery, THIS JOURNAL, **77**, 909 (1955).

[3] E. G. King, *ibid.*, **79**, 2399 (1957).

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