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.

(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).

$Ga_2O_3(\beta)$: $D(286/T) + E(293/T) + 3E(730/T)$ (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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[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.

(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).

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

The measured heat contents are given in Table I, being expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Molecular weights accord with the 1954–55 Report on Atomic Weights.[5]

The data for cobaltous oxide are regular, except in the region adjacent to 298°K., where the heat capacity is decreasing with increasing temperature. The average heat capacity between 298.15 and 402.5°K. (lowest value in Table I) is 12.70 cal./deg. mole, as compared with 13.20, which is the true heat capacity at 298.15°K.[3] This region of decreasing heat capacity, which evidently extends to about 450°K., is a continuation of the upper-temperature part of the heat capacity maximum found by King.[3] The maximum heat capacity occurs at 287.3°K.

Cobalt spinel shows regular behavior to 1000°K. Measurements at higher temperatures were prevented by the beginning of dissociation of the substance, which caused discordant results. No analog of the 900°K.-transformation of magnetite[7] was observed in the temperature range covered.

The data for nickelous oxide show the slope of the heat content–temperature curve to increase rapidly to 525°K., at which point there is an abrupt decrease. This is followed by another decrease in slope at 565°K. These phenomena may be seen in Fig. 1, in which the function

$$D = (H_T - H_{298.15}) - 10.59(T - 298.15)$$

is plotted against temperature. This function, which is the difference between the measured heat content and the heat content that would obtain if the heat capacity remained constant at the 298.15°K. value, is used merely as means of magnification. There is no isothermal heat absorption at either of the critical points.

The data of Tomlinson and co-workers[2] average

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPY INCREMENTS (CAL./DEG. MOLE) ABOVE 298.15°K.

	CoO		Co_3O_4		NiO	
T, °K.	$H_T - H_{298.15}$	$S_T - S_{298.15}$	$H_T - H_{298.15}$	$S_T - S_{298.15}$	$H_T - H_{298.15}$	$S_T - S_{298.15}$
400	1,290	3.72	3,270	9.40	1,165	3.35
500	2,570	6.58	6,850	17.38	2,535	6.39
525	....	...	....	...	2,940(α)	7.18
525	....	...	....	...	2,940(β)	7.18
565	....	...	....	...	3,495(β)	8.20
565	....	...	....	...	3,495(γ)	8.20
600	3,860	8.93	10,660	24.32	3,940	8.97
700	5,160	10.93	14,640	30.45	5,220	10.94
800	6,470	12.68	18,820	36.03	6,500	12.65
900	7,790	14.24	23,300	41.30	7,780	14.16
1000	9,120	15.64	28,250	46.52	9,070	15.52
1100	10,460	16.92	....	...	10,370	16.76
1200	11,820	18.10	....	...	11,700	17.91
1300	13,210	19.21	....	...	13,060	19.00
1400	14,640	20.27	....	...	14,450	20.03
1500	16,100	21.28	....	...	15,860	21.00
1600	17,600	22.25	....	...	17,300	21.93
1700	19,140	23.18	....	...	18,770	22.82
1800	20,730	24.09	....	...	20,260	23.68

(5) E. Wichers, THIS JOURNAL, **78**, 3235 (1956).

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

(7) J. P. Coughlin, E. G. King and K. R. Bonnickson, THIS JOURNAL, **73**, 3891 (1951).

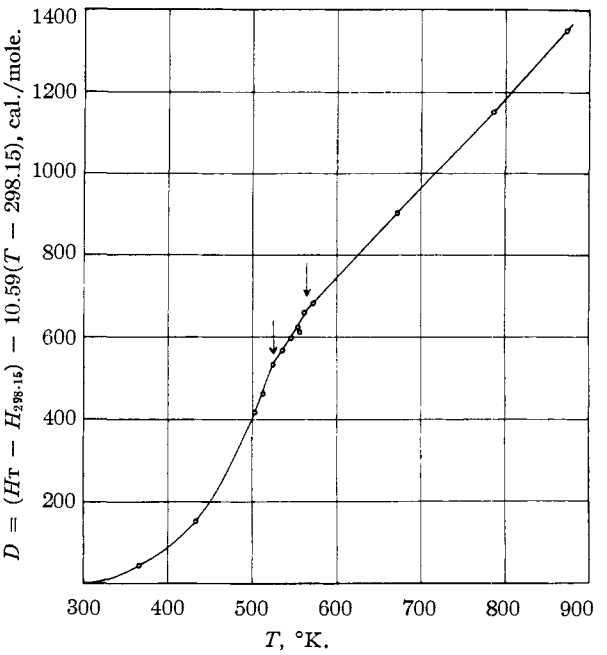

Fig. 1.—Heat content function for nickelous oxide.

1.2% higher than ours but show the same trend with temperature. They report an abrupt change in slope at 523°K., which they assign as the antimagnetic Curie point. Their data also indicate a change in slope near 565°K., when plotted as described above. As pointed out by Tomlinson and co-workers, the data of Kapustinsky and Novosel'tsev[1] are discordant and much too high.

In presenting the data for nickelous oxide in a form suitable for thermodynamic calculations, the letters α, β and γ are used here to designate the substance below 525°K., between 525 and 565°K., and above 565°K.

Table II gives smooth values of the heat content and entropy increments above 298.15°K. The latter were obtained from the former by the method of Kelley,[8] which assures matching values.

The heat-content data in Table II are represented, to within the average deviations indicated, by the equations

CoO(c):

$$H_T - H_{298.15} = 11.54T + 1.02 \times 10^{-3}T^2 - 0.40 \times 10^5T^{-1} - 3397$$

(298–1800°K., 0.5%)

Co_3O_4(c):

$$H_T - H_{298.15} = 30.84T + 8.54 \times 10^{-3}T^2 + 5.72 \times 10^5T^{-1} - 11,873$$

(298–1000°K., 0.5%)

NiO(α):

$$H_T - H_{298.15} = -4.99T + 18.79 \times 10^{-3}T^2 - 3.89 \times 10^5T^{-1} + 1122$$

(298–525°K., 0.4%)

NiO(β):

$$H_T - H_{298.15} = 13.88T - 4347$$

(525–565°K., 0.1%)

NiO(γ):

$$H_T - H_{298.15} = 11.18T + 1.01 \times 10^{-3}T^2 - 3144$$

(565–1800°K., 0.4%)

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(8) K. K. Kelley, U. S. Bur. Mines Bulletin 476, 1949.