TABLE IV

HEATS AND FREE ENERGIES OF FORMATION (KCAL./MOLE)

Substance	From the oxides $\Delta H_{298.15}$	$\Delta F°_{298.15}$	From the elements $\Delta H_{298.15}$	$\Delta F°_{298.15}$
$NaAlO_2$(c)	-20.89 ± 0.78	-21.58 ± 0.80	-270.84 ± 0.17	-255.60 ± 0.19
$LiAlO_2$(c)	-12.88 ± 1.03	-13.50 ± 1.03	-284.33 ± 0.21	-269.49 ± 0.22

formation of lithium aluminate from the component oxides and from the elements, respectively.

$$^1/_2Li_2O(c) + {}^1/_2Al_2O_3(\alpha) = LiAlO_2(c),\quad \Delta H_{298.15} = -12{,}880 \pm 1030 \text{ cal./mole} \qquad (15)$$

$$Li(c) + Al(c) + O_2(g) = LiAlO_2(c),\quad \Delta H_{298.15} = -284{,}330 \pm 210 \text{ cal./mole} \qquad (16)$$

Johnston and Bauer's[13] entropy value for lithium oxide is used, together with entropy data from sources,[2,7,12] to calculate the free energy data in Table IV.

Although no high temperature heat content and entropy increment data are available for these aluminates, the entropies of formation at 298.15°K. indicate that both substances should become increasingly stable with respect to their component oxides with increasing temperature.

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[13] H. L. Johnston and T. W. Bauer, THIS JOURNAL, **73**, 1119 (1951).

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

Heat Capacities at Low Temperatures and Entropies at 298.15° K. of Nickelous Oxide, Cobaltous Oxide and Cobalt Spinel

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Heat capacities of nickelous oxide (NiO), cobaltous oxide (CoO) and cobalt spinel (Co_3O_4) were measured throughout the temperature range 51 to 298°K. The heat capacity of cobaltous oxide has a pronounced maximum at 287.3°K. The entropies at 298.15°K. are 9.08 ± 0.04, 12.66 ± 0.08 and 24.5 ± 0.2 cal./deg. mole, respectively.

This paper presents heat capacity measurements in the temperature range 50 to 298°K. and entropy values at 298.15°K. for crystalline nickelous oxide (NiO), cobaltous oxide (CoO) and cobalt spinel (Co_3O_4). No previous similar data exist for the cobalt compounds. Seltz, DeWitt and McDonald[1] have reported low temperature heat capacity data for nickelous oxide.

Materials.—Nickelous oxide[2] was prepared from reagent grade nickelous nitrate hexahydrate and nickelous sulfate hexahydrate. These materials were dissolved in water and precipitated as basic carbonate with ammonium hydroxide and carbon dioxide. The precipitate was heated slowly to 1000° where it was kept for nine days. Analysis showed 99.96% nickelous oxide, 0.05% cobaltous oxide, 0.01% sodium oxide, and 0.02% acid insoluble. Tests showed no calcium or sulfate. The X-ray diffraction pattern agreed with the ASTM catalog.

Cobaltous oxide was obtained from recrystallized, reagent grade cobaltous sulfate heptahydrate as the starting material. After heating slowly to 1000°, it was maintained at this temperature for nine days. Additional treatment involved heating for 16 hours at 1000° and cooling in nitrogen, followed by an additional six hours *in vacuo* at 1000° with cooling in nitrogen. Analysis showed 78.61% cobalt (theoretical, 78.65%). The X-ray pattern was identical with that in the ASTM catalog.

Recrystallized reagent grade cobalt sulfate heptahydrate was the starting material for preparing cobalt spinel. It was heated in air for 15 days at 850° and 16 hours at 900°, after which it was quenched to room temperature. At this point the product contained too much cobalt (73.71%). It was next heated for 16 hours at 720° and finally for 16 hours at 780°, followed by quenching to room temperature. Analysis of the final product gave 73.40% cobalt, as compared with the theoretical 73.42%. The X-ray diffraction pattern agreed with the ASTM catalog.

Heat Capacity Measurements and Results.—The heat capacity calorimeter has been described.[3] Results are given in defined calories (1 cal. = 4.1840 abs. joules). Weighings were reduced to vacuum and molecular weights were obtained using the 1954–55 Report on Atomic Weights.[4] Sample masses were 275.83 g. of nickelous oxide, 396.86 g. of cobaltous oxide and 161.23 g. of cobalt spinel.

The measurements are tabulated in Table I and plotted in Fig. 1. The heat capacity curves of nickelous oxide and cobalt spinel show a regular behavior over the measured range of temperature. A comparison of the heat capacities of nickel oxide with those of Seltz and co-workers[1] shows the present values to be lower. The difference is 2.0% at 75°K., becomes zero at 125°K., then increases again to 1.5% at 258°K., and finally decreases to 0.1% at 298°K.

Cobaltous oxide possesses a peak with the maximum at 287.3°K., at which point the heat capacity is greater than 17.6 cal./deg. mole. As may be seen in Fig. 1, abnormal heat capacities persist for a wide temperature range both above and below the maximum. At the highest measured temperature (307.6°K.) the heat capacity continues to decrease with increasing temperature. Results labeled (a) in Table I were obtained without temperature gaps. In the immediate neighborhood of the peak, runs with temperature rises of only about one degree

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[1] H. Seltz, B. J. DeWitt and H. J. McDonald, THIS JOURNAL, **62**, 88 (1940).

[2] All three substances were prepared by K. R. Bonnickson, Chemist, Minerals Thermodynamics Experiment Station, Region II, Bureau of Mines.

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

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

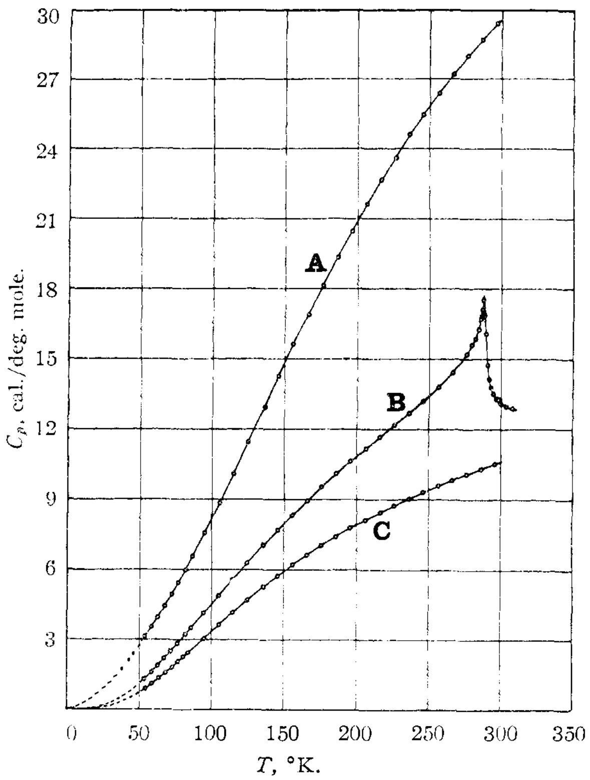

Fig. 1.—Heat capacities: curve A, Co_3O_4; curve B, CoO; curve C, NiO.

TABLE I

HEAT CAPACITIES (CAL./DEG. MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		CoO (mol. wt., 74.94)			
53.61	1.309	165.67	8.939	285.48(a)	16.69
58.27	1.598	175.82	9.526	286.36	16.87
62.80	1.895	185.97	10.12	286.48(a)	17.13
67.20	2.194	195.82	10.63	287.37(a)	17.57
71.72	2.511	206.10	11.16	288.27(a)	16.89
76.31	2.834	215.94	11.67	289.27(a)	16.08
81.76	3.227	225.96	12.19	290.33(a)	14.75
85.71	3.511	235.85	12.69	291.44(a)	14.15
94.37	4.138	245.65	13.19	292.59(a)	13.79
104.79	4.896	256.13	13.79	294.25(a)	13.51
114.22	5.563	266.10	14.43	296.82(a)	13.30
124.28	6.268	276.03	15.19	297.34	13.27
135.71	7.034	279.74(a)	15.60	299.87(a)	13.11
145.57	7.695	282.15(a)	15.89	303.40(a)	12.99
155.66	8.336	284.06(a)	16.28	307.61(a)	12.90
		Co_3O_4 (mol. wt., 240.82)			
54.02	3.153	114.67	10.09	216.33	22.68
58.55	3.544	124.81	11.45	226.40	23.68
63.05	3.952	136.03	12.93	236.23	24.62
67.68	4.439	145.76	14.26	245.77	25.46
72.32	4.938	155.91	15.61	256.47	26.37
76.78	5.446	165.95	16.89	266.42	27.19
81.40	5.955	176.02	18.12	276.33	27.98
86.57	6.554	186.06	19.36	286.92	28.70
94.93	7.568	196.03	20.47	296.34	29.29
104.98	8.850	206.38	21.65		
		NiO (mol. wt., 74.71)			
54.28	0.900	114.57	4.158	216.19	8.457
58.93	1.112	124.60	4.691	225.85	8.762
63.49	1.341	135.88	5.269	236.07	9.050
68.10	1.582	145.55	5.737	245.63	9.306
72.47	1.818	155.86	6.221	256.29	9.597
76.74	2.051	165.78	6.639	266.15	9.845
80.22	2.248	175.84	7.041	276.01	10.08
83.81	2.444	185.78	7.427	286.43	10.32
94.66	3.056	195.94	7.785	295.94	10.55
104.97	3.639	206.13	8.134		

TABLE II

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

	NiO	CoO	Co_3O_4
0–51°K. (extrap.)	0.27	0.42	1.36
51–298.15°K. (measd.)	8.81	12.24	23.18
	9.08 ± 0.04	12.66 ± 0.08	24.5 ± 0.2

were made to better portray the heat capacity curve. This heat capacity maximum is similar to the one found by Todd[5] at 188.5°K. for the compound $Fe_{0.947}O$.

Two separate total heat measurements were made for cobaltous oxide between 280.00 and 294.00°K., enclosing the sharpest part of the peak. The measurements gave identical heat absorptions of 217.9 cal./deg. mole. The runs labeled (a) in Table I also were used (in summation) to obtain this total heat. The latter method gave 219.9 cal./deg. mole, in fair agreement with the total heat runs.

Entropies at 298.15°K.—The entropy of cobaltous oxide between 0 and 51°K. (the extrapolated portion) was calculated from the Debye–Einstein function sum $D(359/T) + E(484/T)$, which fits the measured data within 1.0% between 51 and 100°K. The entropy for the intervals 51–280°K. and 294–298°K. were obtained by graphical integration of a C_p *vs.* log T plots of the data. These increments totaled 11.48 cal./deg. mole. The entropy between 280.00° and 294.00°K. was calculated from the equation

$$\Delta S = \Delta H \frac{\Sigma C_p \Delta T/T}{\Sigma C_p \Delta T}$$

where ΔH is the total heat over the temperature interval and the other two terms were obtained from the consecutive run data marked (a) in Table I. This portion of the entropy was evaluated as 0.76 cal./deg. mole.

The entropy for nickelous oxide below 51°K. was calculated from the function sum $D(422/T) + E(585/T)$, which fits the experimental data below 200°K. within 2.0%. Likewise, the entropy of cobalt spinel below 51°K. was obtained from the function sum $D(219/T) + 3E(485/T) + 3E(926/T)$ which fits the measured data below 200°K. within 1.0%. The entropies between 51 and 298.15°K. for nickelous oxide and cobalt spinel were obtained from C_p *vs.* log T plots.

Table II summarizes the entropy calculations.

The present entropy value at 298.15°K. for nickelous oxide is considered more reliable than the value of 9.24 cal./deg. mole calculated by Kelley[6] from the data of Seltz and co-workers.[1]

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[5] S. S. Todd, THIS JOURNAL, **73**, 3894 (1951).

[6] K. K. Kelley, U. S. Bur. Mines Bulletin 477 (1950).