The Heat Capacity of Anhydrous NiCl₂ from 15 to 300°K. The Antiferromagnetic Anomaly near 52°K. Entropy and Free Energy[1]

BY R. H. BUSEY AND W. F. GIAUQUE

The heat capacity of anhydrous nickelous chloride has been measured from 15 to 300°K. The anomalous region associated with the transition from the antiferromagnetic to the paramagnetic state has been investigated in detail. A maximum was found in the heat capacity near 52°K. which corresponds to the maximum magnetic susceptibility within the accuracy of the magnetic measurements. Thermodynamic properties are given to 300°K. and these in conjunction with the work of Coughlin from 298 to 1336°K. on a sample of the same material complete the thermodynamic description over the range 15 to 1336°K. The entropy was found to be 23.33 cal. deg.⁻¹ mole⁻¹ at 298.16°K.

The low temperature heat capacity of anhydrous nickel chloride reported here was measured to provide values of the entropy and free energy functions in connection with a study of the equilibrium reduction of NiCl₂ by hydrogen. It is also of interest because of the heat effect accompanying the gradual transition from the antiferromagnetic to the paramagnetic state characteristic of higher temperatures.

Since impurities might have a serious effect on the equilibrium measurements, and also on the antiferromagnetic behavior of the substance, high purity material was considered to be of exceptional importance. The preparation of pure anhydrous NiCl₂ was by far the most laborious and time consuming part of the research.

Preparation of NiCl₂.—The nickelous chloride was prepared by a method which was essentially the same as that used by Baxter and Hilton[2] in their work on the atomic weight of nickel. Pyrex glass was used in place of platinum vessels, which were considered unnecessary since the NiCl₂ was finally doubly distilled. Although the starting material contained only 0.01 mole per cent. of cobalt, on a nickel basis, a preliminary purification, using Ilinsky–Knorre's[3] α-nitroso-β-naphthol method, for the separation of small amounts of cobalt was carried out. The procedure followed was that of Mellor and Thompson.[4]

The product was given a preliminary drying at 400° in a stream of anhydrous hydrogen chloride. The sublimation was carried out in a clear quartz tube about 3.7 cm. i.d. and 60 cm. long. The exit end of the quartz tube was reduced to about 0.8 cm. i.d. and pointed downward to end in a 1-mm. bubbler immersed in concentrated sulfuric acid. The hydrogen chloride gas moved through the tube at a rate of about 3 cc. per min. measured at room temperature. Three tube furnaces, each of which was 10 cm. in length, were used in series. The first and third furnaces were operated at 900–1000°. The intermediate furnace was held at 400–450°. A quartz boat containing the nickel chloride to be sublimed was centered in the first furnace. Condensation occurred in the region of the middle furnace. At first it was thought that a single furnace around the boat would suffice; however, colloidal NiCl₂, produced by sudden condensation, was carried out of the tube. The second furnace, at 400°, was added to increase the particle size. This was partially successful but some NiCl₂ was still carried out in colloidal form. The addition of the third furnace, at 1000°, caused essentially complete condensation in the 400° range. The function of the third furnace is as follows: It had been noticed in preliminary experiments that heating with a flame caused a good deal of convection within the tube. In the final arrangement the gas had considerable opportunity for convection during which it passed through a variety of temperatures and evidently had increased opportunity for particle growth.

The hydrogen chloride gas stream was replaced by nitrogen before the sublimed material was removed in a dry-box. A residue of approximately 3 mg., which was probably silica, remained in the boat from a 30-g. sample of NiCl₂ in the first sublimation. All of the material was sublimed twice and there was about 1 mg. of residue after the second sublimation of a 35-g. sample.

Approximately 550 g. of anhydrous crystalline nickelous chloride was prepared. The salt was orange to red in color depending on the crystal size. All subsequent handling of the nickel chloride was carried out in a dry-box.

Analysis of Nickelous Chloride.—The nickelous chloride was analyzed for chloride and nickel content. The chloride was determined by weighing silver chloride dried to constant weight at 325°. The nickel was determined by the dimethylglyoxime method. All weights were corrected to vacuum. The density of NiCl₂ was taken as 3.54 g./ml. as determined by Baxter and Hilton.[2] The density of nickel dimethylglyoxime is not known but was estimated as 2.5 g./ml. The atomic weights were taken as Ni = 58.69, Cl = 35.457, Ag = 107.880. The molecular weight of nickel dimethylglyoxime, NiC₈H₁₄N₄O₂, was taken as 288.914. The chloride analysis is considerably more accurate than that of the nickel.

Two analyses for chloride gave 54.716 and 54.714% compared to the theoretical value of 54.716%. The amount of AgCl weighed was about 10 g. in each case. Two analyses for nickel gave 45.28 and 45.30% compared to the theoretical 45.284%. The amounts of nickel dimethylglyoxime weighed were about 2.5 g.

Calorimetric Apparatus and Procedure.—The calorimetric arrangement was of the type ordinarily used in this Laboratory. It was similar to one described by Giauque and Egan[5] except that the calorimeter was made of copper instead of gold and it did not have the features relating particularly to condensed gases. The gold resistance thermometer was calibrated in terms of a standard thermocouple with the laboratory designation W-26 originally compared to a helium gas thermometer. Both the thermocouple and resistance thermometer were compared directly with the triple and boiling points of both hydrogen and nitrogen, during the present work, by condensing these substances in the insulating vacuum space. H₂, t.p. 13.92°, b.p. 20.36°K.; N₂, t.p. 63.15°, b.p. 77.34°K.; 0°C. was taken as equal to 273.16°K.

One innovation which will be of importance in many future cases concerns the way in which the thermocouple was attached. Previously a small thermocouple well was permanently attached to the calorimeter. Rose's alloy was used in the well to provide thermal contact. It is often difficult to detach the fragile thermocouple in close quarters with such an arrangement, especially since the heat applied to melt the alloy passes rapidly into the calorimeter. However, there is a more important reason for having an alternative method of attachment. When hydrated or other easily decomposed substances are investigated the melting of a fusible alloy without heating the substance above its decomposition temperature presents a serious problem. One method is to cool the sample to a low temperature and then melt the fusible alloy so rapidly that the substance will

(1) This work was supported in part by the Office of Naval Research, U. S. Navy.

(2) G. P. Baxter and F. A. Hilton, THIS JOURNAL, **45**, 694 (1923).

(3) M. Ilinsky and G. von Knorre, *Ber.*, **18**, 699, 2728 (1885); **20**, 283 (1887).

(4) J. W. Mellor and H. V. Thompson, "A Treatise on Quantitative Inorganic Analysis," Charles Griffin and Co., London, 1938, pp. 420-421.

(5) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

not heat above the allowable temperature but such treatment is not desirable especially with a fragile calorimeter.

A detachable thermocouple well arrangement was made in the form of a hollow brass plug with an outside diameter

TABLE I

HEAT CAPACITY OF NiCl₂

0°C. = 273.16°K.; mol. wt. 129.604; C_p, cal. deg.⁻¹ mole⁻¹

$T_{av.}$	C_p	$T_{av.}$	C_p	$T_{av.}$	C_p
Series A		83.48	8.799	181.61	14.99
272.60	16.82	88.75	9.367	187.07	15.16
280.41	16.92	94.07	9.897	192.85	15.32
288.40	17.01	99.49	10.42	198.52	15.47
296.84	17.12	104.95	10.89	204.05	15.62
305.90	17.21	110.45	11.54	210.05	15.75
315.87	17.28	115.84	11.76	216.40	15.90
325.62	17.46	121.35	12.16	222.94	16.03
336.36	17.49	126.77	12.52	229.28	16.14
Series B		132.28	12.86	235.42	16.27
79.91	8.499	138.02	13.17	241.76	16.36
84.56	8.919	143.38	13.46	248.13	16.48
Series C		148.64	13.72	254.41	16.56
61.45	6.204	154.08	13.97	260.89	16.67
65.03	6.583	159.62	14.21	268.00	16.76
69.21	7.130	165.05	14.42	275.23	16.85
73.56	7.659	170.36	14.62	283.07	16.94
78.27	8.201	176.03	14.81		

$T_{av.}$	$\Delta T_{approx.}$	C_p	$T_{av.}$	$\Delta T_{approx.}$	C_p
Series D			Series F		
14.14	0.94	0.417	20.57	1.50	0.839
16.03	1.74	.521	22.35	1.90	0.976
18.34	1.35	.668	24.93	3.19	1.203
20.47	2.31	.822	28.07	3.04	1.515
22.72	1.87	1.000	32.19	4.93	1.978
23.90	3.11	1.105	38.24	3.80	2.831
26.80	2.75	1.376	42.45	4.25	3.535
29.56	2.73	1.668	46.61	3.93	4.410
32.57	3.23	2.025	56.70	2.65	5.683
38.51	3.14	2.884	59.31	2.46	5.931
41.92	3.50	3.471	62.05	2.94	6.222
45.35	3.23	4.126	Series G		
47.85	1.72	4.717	21.56	1.63	0.904
49.27	0.63	5.108	24.16	3.39	1.131
49.93	.68	5.326	27.61	3.45	1.460
50.58	.64	5.550	31.89	4.96	1.949
51.20	.61	5.809	37.22	5.34	2.684
55.36	.87	5.581	43.15	6.23	3.700
56.22	.56	5.696	47.54	2.45	4.636
57.28	.55	5.722	50.04	2.56	5.393
57.83	.54	5.805	51.45	0.14	5.976
58.35	.53	5.846	51.62	.14	6.053
58.90	.52	5.905	51.77	.14	6.144
59.42	.51	5.954	51.91	.14	6.241
59.93	.51	5.992	52.04	.14	6.367
60.44	.50	6.037	52.18	.13	6.498
60.94	.49	6.116	52.32	.13	6.738
61.43	.48	6.177	52.45	.13	6.422
63.15	2.87	6.353	52.59	.14	5.878
Series E			52.96	.59	5.617
57.02	2.65	5.716	53.56	.59	5.527
59.60	2.45	5.963	54.15	.59	5.532
62.16	2.65	6.243	54.73	.58	5.556
			55.79	1.52	5.612
			58.22	3.26	5.829
			61.62	3.53	6.193

of 0.5 cm. and a length of 2.5 cm. The plug had a total taper of 4°. This fitted into a hollow brass cylinder, with matching taper, which was permanently soldered to the calorimeter. The thermocouple junction was left permanently soldered in the well within the plug which could be pulled and held tightly in place by means of a screw and lock washer. A suitable dismantling tool was necessary to force the joint apart when the calorimeter was disassembled.

In the present case there was no reason for not heating the anhydrous nickel chloride; however, it seemed desirable to try out the detachable thermocouple well during an experiment which would not be more than temporarily inconvenienced in case the method failed. The performance was entirely satisfactory.

The Heat Capacity Data.—The observed heat capacity data are given in Table I in the order in which they were measured. The sample weighed 292.614 g. *in vacuo* and the molecular weight of NiCl₂ was taken as 129.604. One defined calorie was taken as 4.1840 absolute joules.

Series D, E, F and G were designed to give information about the anomaly in the heat capacity curve which has a maximum near 52°K. The shape of the curve is characteristic of a coöperative phenomenon and indicates that special care should be taken with respect to slow attainment of equilibrium. In order to test this point the sample was cooled from 77°K. to liquid hydrogen temperatures as rapidly as possible before series D. The calorimetric arrangement is such as to prevent very rapid cooling and the rate was 0.7° min.⁻¹ at 60°K. and 0.4° min.⁻¹ at 40°K.

Measurements of series E were made immediately after those of series D by recooling the sample from 64.5 to 55.7°K. at the average rate of 0.07° min.⁻¹.

Series F was obtained after the sample had been cooled slowly from 60 to 40°K. The cooling rate was 0.07° min.⁻¹ at 60°, 0.09° min.⁻¹ at 50°, and 0.05° min.⁻¹ at 40°K.

Series G was measured for the express purpose of determining the low temperature part of the curve after slow cooling with sufficiently small intervals to determine the shape of the anomalous curve. The cooling rate was 0.12° min.⁻¹ at 60°, 0.13° min.⁻¹ at both 50 and 40°K.

The Anomaly in the Heat Capacity of Nickelous Chloride.

—Figure 1 shows the heat capacity data between 40 and 65°K. Series G shows that the heat capacity rises rather rapidly on the low temperature side and then decreases rather abruptly from the maximum value. This is typical of curves obtained in various cases of coöperative phenomena associated with effects ranging from molecular rotation within crystals, ferromagnetism, antiferromagnetism or liquid helium II.

The magnetic susceptibility of nickelous chloride[6-8] increases with decreasing temperature until it reaches a maximum which coincides with the heat capacity anomaly within the limit of error of the magnetic data. Below the transition region, (frequently and incorrectly referred to as the "Curie point" or "Curie temperature") the susceptibility decreases slightly but is almost without temperature coefficient. This means that magnetization at very low temperatures may be thought of as an ordered mechanical process without an appreciable entropy change. This is consistent with the thermodynamic formula

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial I}{\partial T}\right)_H = 0 \text{ experimentally} \qquad (1)$$

where I, H and S refer to the intensity of magnetization, field strength and entropy, respectively. The entropy of NiCl₂ should approach zero at very low temperatures unless some disorder of molecular

(6) H. R. Woltjer, *Comm. Phys. Lab. Univ. of Leiden*, No. 173b (1925).

(7) H. R. Woltjer and H. Kamerlingh Onnes, *ibid.*, No. 173c.

(8) C. Starr, F. Bitter and A. R. Kaufmann, *Phys. Rev.*, **58**, 977 (1940).

dimensions should be frozen in and there is no reason to suspect this. Neel,[9] Landau[10] and others[11,12] have suggested that spontaneously magnetized layers of atoms, oppositely oriented, alternate throughout the crystal and this appears to agree with all the known facts. Such an arrangement has been proved recently for the case of MnO and several other similar magnetic oxides by the very interesting neutron diffraction experiments of Shull, Strauser and Wollan.[13]

The calorimetric behavior of the sample indicates that the processes in the transition region are reversible to a high degree of accuracy. Several points between 50 and 57° in series D, which followed rapid cooling, do not quite fall on the curve within the

TABLE II

THERMODYNAMIC PROPERTIES OF NiCl₂

0°C. = 273.16; mol. wt. 129.604; cal. deg.$^{-1}$ mole^{-1}

T	C_p	$S°$	$-\dfrac{F°-H_0^0}{T}$	$\dfrac{H°-H_0^0}{T}$
15	0.461	0.168	0.053	0.115
20	0.787	0.344	.102	.242
25	1.206	0.563	.172	.391
30	1.719	0.826	.258	.568
35	2.352	1.140	.363	.777
40	3.126	1.503	.482	1.021
45	4.052	1.923	.619	1.304
50	5.385	2.413	.773	1.640
51	5.766	2.523	.807	1.716
52	6.321	2.640	.841	1.799
52.35	6.825	2.683	.853	1.830
53	5.586	2.757	.876	1.881
54	5.529	2.860	.911	1.949
55	5.569	2.962	.948	2.014
60	6.017	3.464	1.137	2.327
70	7.216	4.479	1.541	2.938
80	8.411	5.522	1.973	3.549
90	9.492	6.575	2.426	4.149
100	10.46	7.626	2.894	4.732
110	11.32	8.664	3.371	5.293
120	12.07	9.681	3.855	5.826
130	12.72	10.673	4.341	6.332
140	13.29	11.637	4.828	6.809
150	13.78	12.571	5.313	7.258
160	14.22	13.475	5.795	7.680
170	14.60	14.349	6.273	8.076
180	14.92	15.192	6.745	8.447
190	15.24	16.008	7.212	8.796
200	15.52	16.797	7.672	9.125
210	15.76	17.560	8.123	9.437
220	15.97	18.298	8.569	9.729
230	16.16	19.012	9.007	10.005
240	16.34	19.703	9.438	10.265
250	16.50	20.374	9.864	10.510
260	16.65	21.023	10.279	10.744
270	16.79	21.654	10.688	10.966
280	16.91	22.266	11.091	11.175
290	17.03	22.861	11.486	11.375
298.16	17.13	23.334	11.803	11.531
300	17.15	23.440	11.874	11.566

(9) L. Neel, *Ann. phys.*, **18**, 5 (1932).

(10) L. Landau, *Phys. Z. Sowjetunion*, **4**, 675 (1933).

(11) F. Bitter, *Phys. Rev.*, **54**, 79 (1938).

(12) C. Starr, *ibid.*, **58**, 984 (1940).

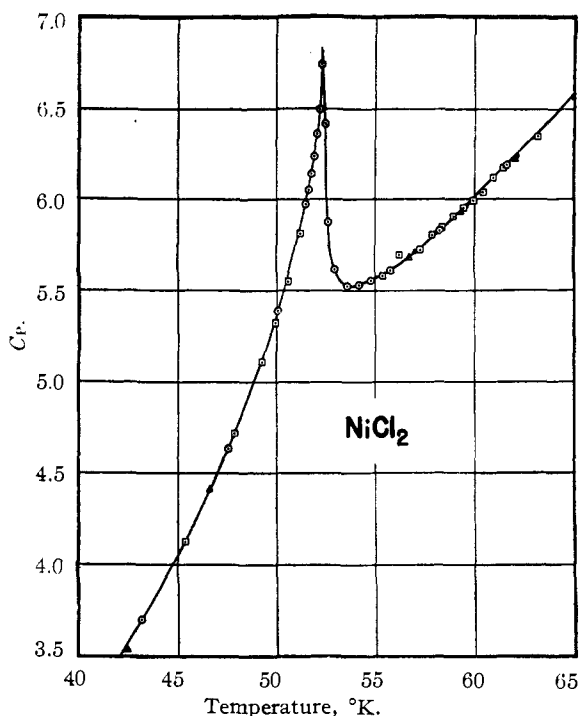(13) C. G. Shull, W. A. Strauser and E. O. Wollan, *ibid.*, **83**, 333 (1951).

Fig. 1.—Anomaly in heat capacity of NiCl₂ (calories per degree per mole): □, series D; ●, series E; △, series F; ○, series G.

limit of error of measurement, however the difference is trivial.

Accuracy and Comparison with Other Measurements.—At 15°K. the results may be in error by 5%, at 20° by 1%, and from 25 to 40° by two- or three-tenths of a per cent. It is difficult to make a comparison of the runs of various lengths in the region of the anomaly but the smooth curve through the data in this region should be accurate to within 0.5%. Above 65° a smooth curve should be accurate to about 0.1% except near 300°K. where increased heat leak may introduce an error of several tenths of a per cent.

The only previous measurements of the heat capacity of nickelous chloride are those of Trapeznikowa, Schubnikow and Miljutin,[14] who covered the range from 14 to 150°K. They used a glass calorimeter and a platinum thermometer-heater.

The data obtained in this research do not confirm the results of the above investigators. Their results are 60% higher at 15°, 30% higher at 20°, 20% at 30° and approximately 10% higher in the range 40 to 130°K. Their heat capacity curve has two maxima, one at 49.6°K. and the other at 57–58°. They give a chloride analysis of 54.49% against 54.72% theoretical. If the difference is due to the presence of basic chloride one might expect a disturbance in the antiferromagnetic transition. However, no reasonable amount of impurity could explain the great differences in the measurements and we are forced to conclude that the glass calorimeter of T., S. and M. did not attain thermal equilibrium with their thermometer.

Thermodynamic Properties of Nickelous Chloride.—The thermodynamic properties of nickelous

(14) O. Trapeznikowa, L. Schubnikow and G. Miljutin, *Phys. Z. Sowjetunion*, **9**, 237 (1936).

chloride are given in Table II. The values of entropy and free energy do not include the effects of nuclear spin or isotopes.

Through the coöperation of Dr. K. K. Kelley of the Pacific Experiment Station of the U. S. Bureau of Mines, a sample of the nickelous chloride prepared in this research was measured between 298 and 1336°K. The results have been published by Coughlin[15] who gives tables of the increments of the thermodynamic properties above 298.16°K.

(15) J. P. Coughlin, This Journal, 73, 5314 (1951).

To extend the present results to the higher temperatures

$$S_T^\circ = 23.33 + (S_T^\circ - S_{298.16}^\circ)_{\text{Coughlin}}$$

$$\frac{H_T^\circ - H_0^0}{T} = \frac{11.531 \times 298.16 + (H_T^\circ - H_{2\ 8.16}^\circ)_{\text{Coughlin}}}{T}$$

$$\frac{F_T^\circ - H_0^0}{T} = \frac{H_T^\circ - H_0^0}{T} - S_T^\circ$$

We thank Dr. J. E. Kunzler for assistance with the heat capacity measurements.

Berkeley, California

Heats of Formation of Manganous Metasilicate (Rhodonite) and Ferrous Orthosilicate (Fayalite)

By E. G. King

The heats of formation of manganous metasilicate and ferrous orthosilicate were obtained by hydrofluoric acid solution calorimetry. The results are, respectively, $\Delta H_{298.16} = -308.22 \pm 0.34$ and $\Delta H_{298.16} = -346.0 \pm 1.1$ kcal./mole (heats of formation from the elements); and $\Delta H_{298.16} = -5.92 \pm 0.17$ and $\Delta H_{298.16} = -8.2 \pm 1.1$ kcal./mole (heats of formation from the oxides).

Recent papers[1,2] from this Laboratory reported heat of formation values at 298.16°K. for silicates of calcium, magnesium and zinc. The present paper gives the results of similar investigations of manganous metasilicate (rhodonite) and ferrous orthosilicate (fayalite).

Method and Materials.—The hydrofluoric acid solution calorimeter and method of operation were described previously.[1,2]

Reagent-grade hydrofluoric acid, 20.1% by weight, was used as the solution medium. The calorimeter was operated at 73.7° for the manganous silicate measurements and at 60.0° for ferrous silicate measurements.

All samples were dropped from 25° into the calorimeter at operating temperature. The samples were enclosed in gelatin capsules, for which corrections were determined by separate experiments. In each determination, 940.1 g. of the acid was employed. The masses of all other materials conformed stoichiometrically with 0.7420 g. of quartz.

The time required to reach thermal equilibrium ranged from 10 to 30 min., depending upon the substance being dissolved. Likewise, the calorimeter temperature rises ranged from 0.15 to 0.65°.

The calorimeter was calibrated several times during the course of each set of measurements, by supplying a measured amount of electrical energy and accurately determining the corresponding temperature rise.

Preparations and analyses of the manganous metasilicate (rhodonite) and ferrous orthosilicate (fayalite) used in this work were described by Kelley.[3]

Anhydrous ferrous chloride was prepared by the method of Kelley and Moore,[4] except that a hydrochloric acid solution of pure electrolytic iron (99.96%) was used as a starting material instead of ferrous chloride tetrahydrate. Analysis of the product gave 44.15% iron and 55.91% chlorine, as compared with the theoretical 44.06 and 55.94%.

The quartz was the same as that employed in previous work.[1,2] It was finely ground, water elutriated, and dried at 180°. Correction in the measurements was made for 0.4% residual moisture content.

Manganous oxide was prepared from the pure dioxide

(1) D. R. Torgeson and Th. G. Sahama, This Journal, 70, 2156 (1948).

(2) E. G. King, ibid., 73, 656 (1951).

(3) K. K. Kelley, ibid., 63, 2750 (1941).

(4) K. K. Kelley and G. E. Moore, ibid., 65, 1264 (1943).

described by Kelley and Moore[5] by hydrogen reduction at 1100°. Analysis gave a purity of 99.92%.

The hydrochloric acid solution, which enters into the ferrous silicate measurements, was standardized against sodium carbonate prepared from reagent grade sodium bicarbonate. It analyzed 25.85% hydrogen chloride, corresponding to HCl·5.806H₂O.

Measurements and Results.—All thermal values are expressed in defined calories (1 cal. = 4.1833 int. joules). All weights were reduced to vacuum, and all molecular weights accord with the 1949 International Atomic Weights.

Table I presents schematically the process used in obtaining the heat of formation of manganous metasilicate.

Table I

HEAT OF FORMATION OF MnSiO₃(RHODONITE)(CAL./MOLE)

Reaction	ΔH	Uncer-tainty
(1) MnSiO₃ (c, 25°) + 8H⁺ (sol., 73.7°) + 6F⁻ (sol., 73.7°) → Mn⁺⁺ (sol., 73.7°) + H₂SiF₆ (sol., 73.7°) + 3H₂O (sol., 73.7°)	−56,300	80
(2) SiO₂ (c, 25°) + 6H⁺ (sol., 73.7°) + 6F⁻ (sol., 73.7°) → H₂SiF₆ (sol., 73.7°) + 2H₂O (sol., 73.7°)	−33,290	80
(3) MnO (c, 25°) + 2H⁺ (sol., 73.7°) → Mn⁺⁺ (sol., 73.7°) + H₂O (sol., 73.7°)	−28,930	130
(4) MnO (c, 25°) + SiO₂ (c, 25°) → MnSiO₃ (c, 25°)	−5,920	170

$$\Delta H_4 = \Delta H_2 + \Delta H_3 - \Delta H_1$$

Six determinations of the heat of reaction (1) were made, the results being −56,250, −56,450, −56,180, −56,260, −56,290 and −56,390 cal. The mean value is −56,300 ± 80 cal.

The heat of reaction (2) was measured in an earlier research,[2] under identical conditions, as −33,290 ± 80 cal.

Reaction (3) was conducted after first dissolving the amount of quartz required by reaction (2).

(5) K. K. Kelley and G. E. Moore, ibid., 65, 782 (1943).