The High Temperature Heat Content of Nickel Oxide

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Differential thermal analysis measurements made in this Laboratory on nickel oxide showed an endotherm at 250°.[1] Magnetic susceptibility[2] and dilatometric measurements[3] by other investigators have shown anomalies at about the same temperature. An X-ray diffraction study[4] indicated that the structure of nickel oxide changed from rhombohedral to face-centered cubic at some temperature below 275°. Since other metal oxides have exhibited specific heat anomalies at the antiferromagnetic Curie temperatures,[5,6] it was suspected that the endotherm found in the differential thermal analysis was due to a specific heat anomaly. The only high temperature heat capacity or heat content measurements on nickel oxide were those of Regnault[7] (1841) and Kapustinsky and Novosel'tsev[8] (1938). The early work was very meager and considered unreliable. In the later work, heat contents were measured at too wide temperature intervals to detect any anomaly. Accordingly, it was decided to confirm the heat capacity anomaly by measuring the heat content of nickel oxide over the range 0–800°, with particular emphasis on the region 200–300°.

Material.—The several samples of nickel oxide used in this investigation were prepared by the decomposition of Mallinckrodt nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$. After decomposition, the samples were maintained at 1000° for eight hours. This led to some sintering and consequent stabilization of the nickel oxide. As a result of this treatment, the samples showed no tendency to pick up excess oxygen, and remained bright green during the entire investigation. Analyses of the oxide samples showed nickel contents of 78.51 and 78.54% compared with 78.58% theoretical. Spectrographic analyses detected silicon as the only impurity present in the range 0.01–0.1%.

Apparatus.—The ice calorimeter and furnace used in this work were essentially similar to those developed by Ginnings[9] and co-workers at the National Bureau of Standards.

Temperatures were measured with a platinum-platinum-10% rhodium thermocouple calibrated against National Bureau of Standards certified freezing point metal baths for the high temperatures, and at the ice and benzoic acid points for the low temperatures.

The calibration factor of the calorimeter was checked by determination of the heat content of pure Al_2O_3 (synthetic sapphire) at several temperatures. Within the experimental error, the values obtained were in excellent agreement with those of Ginnings.[9]

Experimental Results

The measured heat content data, expressed in calories per mole, are listed in Table I. These values are based on 74.69 as the molecular weight of nickel oxide.

TABLE I

MEASURED HEAT CONTENTS ABOVE 273.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{273.16}$	T, °K.	$H_T - H_{273.16}$	T, °K.	$H_T - H_{273.16}$
370.9	1080	537.1	3391	642.9	4813
424.0	1744	551.9	3612	672.3	5192
471.9	2427	552.3	3604	672.9	5184
474.8	2455	563.1	3754	723.5	5833
483.2	2583	573.0	3896	775.3	6522
502.4	2860	573.1	3901	798.6	6812
513.4	3033	573.2	3884	853.5	7552
516.1	3078	619.0	4494	874.8	7780
518.0	3106	620.8	4510	970.5	9077
519.1	3142	642.7	4808	1107.6	10772
523.3	3192				

Seltz, *et al.*,[10] have measured the heat capacity of nickel oxide in the range 68–296°K. From a smoothed plot of their data, a value of 10.14 cal./deg. mole was selected for the heat capacity at 273.16°K. Taking this as a base, the experimental data were treated by the method of Shomate.[11]

The data are well represented by the straight line Shomate plot up to the estimated antiferromagnetic Curie temperature of 523°K. The heat content equation was found to be

$$H_T - H_{273.16} = 0.4257T + 1.42 \times 10^{-2}T^2 - 1.46 \times 10^5 T^{-1} - 641.3 \text{ (cal./mole).}$$

Differentiating with respect to temperature gives for the heat capacity

$$C_p = 0.4257 + 2.84 \times 10^{-2}T + 1.46 \times 10^5 T^{-2} \text{ (cal./deg. mole).}$$

The average deviation of the experimental heat contents from those calculated from the above equation is 5.7 cal./mole (0.24%).

Heat content data above 523°K. deviate sharply from the straight line Shomate plot. This is to be expected if an anomaly occurs around this temperature. A more sensitive determination of the temperature of the anomaly is obtained by plotting the mean heat capacity above a base temperature against the temperature. The closer the base temperature is to the temperature of the anomaly, the sharper will be the discontinuity. Comparison of several plots of this type indicates that the temperature of the anomaly is very close to 523°K. (250°C.). This temperature, then, will be considered the Néel or antiferromagnetic Curie temperature.

Above 620°K., the heat content appears to vary linearly with temperature. A least squares analysis of the data yields the equation

$$H_T - H_{273.16} = 12.91T - 3494 \text{ (cal./mole)}$$

which upon differentiation with respect to temperature gives for the heat capacity

$$C_p = 12.91 \text{ cal./deg. mole}$$

The average deviation of the experimental heat contents from the calculated values is 14.4 cal./mole (0.20%).

The heat capacity of nickel oxide decreases rapidly from the high value at the Néel point (523°K.)

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[1] R. G. Hay, unpublished work.

[2] M. Foëx and C. H. La Blanchetais, *Compt. rend.*, **228**, 1579 (1949).

[3] M. Foëx, *ibid.*, **227**, 193 (1948).

[4] H. P. Rooksby, *Acta Cryst.*, **1**, 226 (1948).

[5] R. W. Millar, THIS JOURNAL, **50**, 1875 (1928).

[6] R. W. Millar, *ibid.*, **51**, 215 (1929).

[7] V. Regnault, *Poggendorf's Ann.*, **53**, 60 (1841).

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

[9] D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583 (1947).

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

[11] C. H. Shomate, *ibid.*, **66**, 928 (1944).

to the lower constant value above 620°K. This behavior cannot be expressed by the usual type of power series equation for heat capacity. Accordingly, no attempt was made to fit the measured heat contents to an equation for this region. The experimental values were smoothed to give a good fit with the data above and below this region. The average deviation of the smoothed values from the experimental heat contents is 7.7 cal./mole (0.21%). Heat capacities in this region were determined by graphical differentiation of the smoothed data.

The heat content measurements of Kapustinsky and Novosel'tsev[8] were made over the temperature range 295–1395°K. with temperature intervals as large as 275°K. No indication of a specific heat anomaly was found. Mean specific heats, $H_t - H_0/t$, calculated from their data do not yield a smooth fit with the low temperature data of Seltz, *et al.*,[10] and in addition, are some 10% larger than those of this research. These results are shown graphically in Fig. 1. Inasmuch as the apparatus and method of this research gave excellent checks with the Bureau of Standards for the heat content of Al_2O_3, we consider our data to be more reliable.

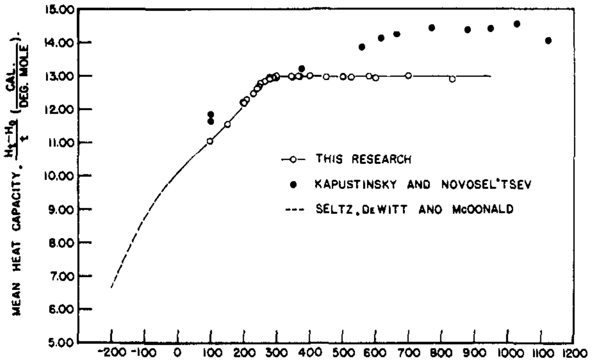

Fig. 1.—Mean heat capacity of nickel oxide.

Thermodynamic Properties.—In Table II are summarized the thermodynamic properties of NiO calculated at intervals of 50°. The values of $H_T - H_0$, C_p and $S_T - S_0$ for 273.16°K. were calculated from the data of Seltz, *et al.*[10]

Table II

Thermodynamic Properties of NiO

T, °K.	$H_T - H_0$, cal./mole	C_p, cal./deg. mole	$S_T - S_0$, cal./deg. mole	$-(F_T - H_0)$ T, cal./deg./mole
273.16	1374	10.14	8.33	3.30
300.0	1652	10.57	9.30	3.79
350.0	2204	11.56	11.00	4.70
400.0	2810	12.70	12.62	5.59
450.0	3475	13.93	14.18	6.46
500.0	4204	15.21	15.72	7.31
523.16[a]	4563	15.82	16.42	7.70
550.0	4953	13.9	17.15	8.14
600.0	5623	13.1	18.31	8.94
650.0	6270	12.91	19.34	9.69
700.0	6916	12.91	20.30	10.42
750.0	7561	12.91	21.19	11.11
800.0	8207	12.91	22.04	11.78
850.0	8852	12.91	22.82	12.41
900.0	9498	12.91	23.56	13.01
950.0	10143	12.91	24.26	13.58
1000.0	10789	12.91	24.92	14.13
1050.0	11434	12.91	25.55	14.66
1100.0	12080	12.91	26.15	15.17

[a] Antiferromagnetic Curie point.

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The Free-radical Catalyzed Addition of Alcohols and Aldehydes to Perfluoroölefins[1]

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Terminally unsaturated perfluoroölefins containing three or more carbon atoms have been found to undergo a free radical catalyzed addition with alcohols and aldehydes to give good yields of adducts. The addition of an alcohol RCH_2OH to $R_fCF{=}CF_2$ yielded the fluorinated alcohol, R_fCFHCF_2CHROH. The aldehyde addition product was identified as the ketone, $R_fCFHCF_2CO{-}R$. No telomerization was observed.

The synthesis of terminally unsaturated perfluoroölefins in high yield by the pyrolysis of the salts of the perfluorocarboxylic acids[2,3] has made many of these olefins available for the investigation of their chemical reactions. While many base-catalyzed nucleophilic addition reactions of these perfluoroölefins have been reported, the investigation of the free radical catalyzed addition of organic compounds has received less attention. Hanford and Joyce in a series of patents[4] have disclosed the free radical catalyzed addition of alcohols, carboxyl compounds, ethers and hydrocarbons to C_2F_4 to obtain $H(CF_2CF_2)_nZ$, where n ranges from one up to as high as twenty-five, and Z is the radical formed from the organic reactant. The structures of the compounds formed from these reactions were not reported. The addition

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[1] Presented before the Fluorine Symposium, 124th Meeting of the American Chemical Society, Chicago, Ill., 1953.

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[3] J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smith, *ibid.*, 75, 4525 (1953).

[4] W. E. Hanford (to du Pont), U. S. Patent 2,411,158 (November 19, 1946); W. E. Hanford (to du Pont), U. S. Patent 2,411,159 (November 19, 1946); W. E. Hanford (to du Pont), U. S. Patent 2,433,844 (January 6, 1948); R. M. Joyce (to du Pont), U. S. Patent 2,559,638 (July 10, 1951).