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Heat Capacity of NiF₂ from 12 to 300°K. Thermodynamic Functions of NiF₂. The Thermal Anomaly Associated with the Antiferromagnetic Ordering

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The heat capacity of NiF₂ has been measured calorimetrically between 12 and 300°K. There is an anomaly in heat capacity rising to a maximum of 9.23 cal deg⁻¹ mole⁻¹ at 73.22°K. The anomaly is associated with the antiferromagnetic ordering of the magnetic moments of the nickel ions. Values of heat capacity, entropy, enthalpy, and free energy are tabulated at selected temperatures. The entropy at 298.16°K is 17.59 ± 0.04 cal deg⁻¹ mole⁻¹. For the reaction NiF₂+H₂=Ni+2HF, $\Delta H_0^0 = 29.56 \pm 0.20$ kcal and $\Delta H^0 = 30.06 \pm 0.20$ kcal at 298.16°K.

HE anhydrous difluorides of manganese, iron, cobalt, nickel, and zinc form an isomorphous series of compounds in which the number of 3d electrons increases from five in MnF_2 to the completed shell of ten in ZnF₂. The crystal structure of these fluorides is of the rutile type, space group D^{14}_{4h} -P4/mnm, and the lattice parameters¹ do not change radically in going from one compound to another. Because they possess an incompletely filled 3d shell, MnF_2 , FeF₂, CoF₂, and NiF₂ are paramagnetic and at room temperature there is an appreciable contribution to their entropy arising from the random distribution of the magnetic ions among low-lying electronic states. The mechanism of the loss of this electronic entropy at lower temperature is a cooperative one, involving interactions between neighboring magnetic ions. Measurements of the magnetic susceptibility,^{2,3} magnetic anisotropy,⁴ and of the structure by neutron diffraction⁵ indicate that the low temperature ordered state is an antiferromagnetic⁶ one with the spins aligned parallel and antiparallel to the fourfold axis of the tetragonal crystal. In NiF₂ there is evidence from the neutron diffraction pattern⁵ that the spins are cocked slightly away from strict alignment along the tetragonal axis and the magnetic anisotropy results⁴ indicate that this cocking is such as to lead to a small ferromagnetic moment at temperatures below that at which longrange order begins.

An approximate molecular field theory of the ordering process in an antiferromagnetic material, equivalent to the Weiss-Heisenberg theory of ferromagnetism, has been given by Van Vleck.7 This theory neglects the

short-range order existing above the temperature of maximum heat capacity. Measurements of low temperature heat capacity are a powerful experimental tool for the investigation of the ordering process. Through the use of the third law of thermodynamics the entropy at various temperatures may be calculated directly from the heat capacity measurements, and the entropy in turn is directly related to the disorder. The observed entropy, however, arises both from the disordering of the magnetic system and from the lattice vibrations, and to focus attention on the magnetic system, it is necessary to subtract the lattice entropy. Measurements of the low-temperature heat capacity of MnF₂ have been reported⁸ previously. A brief note calling attention to the thermal anomalies found in FeF2, CoF2, and NiF2 has been published.9 The present paper presents in detail the measurements on NiF₂. Results on FeF₂, CoF₂, and the isomorphous diamagnetic compound ZnF2, which was measured to assist in the estimation of the lattice entropy in the antiferromagnetic fluorides, will be given in later papers.

APPARATUS AND CALORIMETRIC PROCEDURES

For the measurement of heat capacity a vacuum calorimeter surrounded by a massive isothermal shield was used. The construction of this shield and of the external parts of the cryostat were similar to that described by Giauque and Egan,¹⁰ except that the seal at the top of the vacuum can was made with Rose metal solder rather than by a mechanical joint.

The calorimeter consisted of a copper cylinder, 10.8 cm long, 4.5 cm diameter, and 0.25 mm wall, closed at the top and bottom with end caps of 0.5 mm wall thickness. The filling tube, a short piece of 0.95 cm cupronickel tubing, is at the bottom when the calorimeter is in the cryostat. All joints in the calorimeter are silver-soldered except the cap on the filling tube which was soft-soldered. This cap contained a small pinhole through which air was evacuated and helium exchange gas introduced after the sample was in the calorimeter

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<sup>and Dye Corporation Fellow 1952-1953.
¹ J. W. Stout and Stanley A. Reed, J. Am. Chem. Soc. 76, 5279 (1954). References to earlier work are given in reference 1.
² (a) W. J. de Haas and B. H. Schultz, Physica 6, 481 (1939);
(b) de Haas, Schultz, and Koolhaas, Physica 7, 57 (1940).
³ (a) H. Bizette and B. Tsai, Compt. rend. 212, 119 (1941);
(b) H. Bizette, Ann phys. [12] 1, 295 (1946).
⁴ (a) M. Griffel and J. W. Stout, J. Chem. Phys. 18, 1455 (1950);
(b) J. W. Stout and L. M. Matarrese, Revs. Modern Phys. 25, 338 (1953); (c) L. M. Matarrese and J. W. Stout, Phys. Rev. 94, 1792 (1954).</sup> 1792 (1954)

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⁶ R. A. Erickson, Phys. Rev. 90, 779 (1953).
⁶ See (a) L. Néel, Proc. Phys. Soc. (London) A65, 869 (1952);
(b) A. B. Lidiard, Repts. Progr. in Phys. 17, 201 (1954).
⁷ J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).

⁸ J. W. Stout and H. E. Adams, J. Am. Chem. Soc. 64, 1535 (1942).

 ⁹ J. W. Stout and E. Catalano, Phys. Rev. 92, 1575 (1953).
 ¹⁰ W. F. Giauque and C. J. Egan, J. Chem. Phys. 5, 45 (1937).

and the cap soldered on the filling tube. After the introduction of helium gas, the pinhole was sealed with Rose metal. The resistance thermometer-heater, sealed in its case, slipped into a dead-end copper tube open at the top, centrally located in the calorimeter and extending for about two-thirds of its length. Thermal contact between the thermometer-heater and the calorimeter was made with a solder (49 percent Bi, 18 percent Pb, 15 percent Sn, 18 percent In) melting at 58°C. This solder adhered well to the copper surfaces and was much more satisfactory than Wood's metal which we had used at first. The outside of the calorimeter was gold plated. The calorimeter had a capacity of 152 ml and, including the resistance thermometer, weighed 103 g.

The resistance thermometer-heater, made of pure platinum wire, is similar to the strain-free type described by Meyers.¹¹ The platinum wire, 0.07 mm diameter, was wound on a 0.28 mm diameter steel piano wire. The steel wire was then dissolved in dilute HCl and the helical platinum coil, stretched slightly so no turns touched, was wound on a mica cross. The platinum coil mounted on the mica cross was annealed in helium for 24 hours at 450°C. It was then inserted into the thermometer case, made of a 0.25 mm wall copper tube. The two ends of the thermometer wire were welded to heavy Pt leads, 19×0.64 mm, which were soldered inside the two Kovar tubes of a commercial "Stupakoff" ceramic seal which was in turn soldered in the top of the thermometer case. We adopted this procedure after unsatisfactory attempts to obtain a Pt-glass seal which did not develop cracks over a period of time. A pinhole was left in the bottom of the thermometer case for pumping and filling with helium gas. After assembly of the thermometer its resistance was measured at the triple point of water and it was annealed several times, with intervening checks of the triple point resistance, by passing currents sufficient to raise the temperature to 450°C through the wire while the case was evacuated and immersed in liquid nitrogen. Helium at one atmosphere was then introduced into the thermometer case and the pinhole sealed with solder. The thermometer was calibrated over the range 12 to 300°K against a laboratory standard Leeds and Northrup 25 ohm platinum resistance thermometer which had been calibrated by the Bureau of Standards. The weight of the thermometer and case was 13 g. The ice point resistance was 183.12 ohms and the resistance at 12°K had dropped to 0.242 ohm.

The electrical measurements of current and potential drop in the resistance thermometer-heater and of the emf of copper-constantan thermocouples used for rough control of the temperature of the shield and bath were made with an autocalibrated White double potentiometer in conjunction with a high sensitivity Leeds and Northrup galvanometer and calibrated standard cells, standard resistances, and voltage divider. The energy input was automatically started and stopped with a timer similar to that described by Johnston.12

The heat capacity of the empty calorimeter was measured in a separate series of experiments. The heat capacity measurements were further corrected for the changes in amount of helium gas and solder compared to the empty runs, for energy developed in the 0.013 $\times 2.5$ cm platinum leads connecting the heater leads to the heavy copper wires in thermal contact with the shield, and for small effects associated with nonlinearity with time in the rise of temperature during energy input. A more important correction at the highest temperatures arises from finite thermal resistance within the calorimeter. When heat is entering or leaving the calorimeter, during the fore and after rating periods, a steady-state temperature gradient may be established between the thermometer and the mean temperature of the sample. If, for example, the shield temperature is intermediate between the temperature of the calorimeter before and after energy input this gradient will change sign in the fore and after periods and the temperature rise of the thermometer will not be identical with that of the mean sample. A similar correction arises to the heat exchange between calorimeter and shield during energy input since the temperature of that part of the calorimeter exchanging energy with the surroundings is not identical with the temperature it would have if thermal equilibrium were instantaneous. This correction has been treated by Giauque and Wiebe13 for a calorimeter where the thermometer-heater is wound on the outside and it may be assumed that the temperature of the heater wire is that of the outside of the calorimeter. This is not the case in our calorimeter and we therefore determined experimentally the effect of a change of shield temperature upon the resistance of the thermometer and used these data to make the correction.

In our calorimeter the thermometer is in the center and so protected from direct heat exchange by radiation or gas conduction with the shield. Thus in the measurements on the empty calorimeter the observed rise in temperature of the thermometer is slightly greater than that of the mean (weighted according to heat capacity) temperature rise of the calorimeter and a positive correction must be made to the heat capacity. When the calorimeter is filled with sample it is possible for the correction to be either positive or negative, since, depending on the values of the thermal conductances between various parts of the calorimeter and thermometer and the distribution of heat capacity, the temperature rise of the thermometer may be greater or less than the mean temperature rise of the calorimeter. It was therefore necessary to determine experi-

 ¹² H. L. Johnston, J. Opt. Soc. Am. 17, 381 (1928).
 ¹³ W. F. Giauque and R. Wiebe, J. Am. Chem. Soc. 50, 101 (1928).

¹¹ C. H. Meyers, J. Research Natl. Bur. Standards 9, 807 (1932).

TABLE I. The heat capacity of NiF₂. 0°C=273.16°K. Molecular weight 96.69.

^T Av °K	$\begin{array}{c} \text{Approx} \\ \Delta T \end{array}$	$\Delta H/\Delta T$ cal deg ⁻¹ mole ⁻¹	T _{AV} °K	$\begin{array}{c} \text{Approx} \\ \Delta T \end{array}$	$\Delta H/\Delta T$ cal deg ⁻¹ mole ⁻¹
	SERIES I		5	ERIES V	•
81.52	2.91	5.959	55.69	4 70	4 744
84.63	3.29	6.058	60.27	4.46	5.063
88.35	4.09	6.229	63.73	2.54	5.749
	SEDTES II		66.27	2.47	6.315
	SERIES II		68.72	2.39	6.951
53.13	4.21	3.835	73.05	1.73	7.058
57.39 62.27	4.29	4.545	73.84	0.00	7.041
66.72	3.42	6.430	74.51	0.64	6.460
69.92	2.97	7.346	75.16	0.66	6.246
73.33	3.83	7.655	75.88	0.78	6.120
77.68	4.79	6.012	78.29	1.35	0.048 5 070
02.32	4.47	5.987	80.10	2.26	5.944
5	SERIES II	I	83.25	4.04	6.004
88 78 3 06 6 257					
93.09	4.66	6.484	S	ERIES VI	[
98.05	5.15	6.796	72.636	0.249	8.72
103.01	4.77	7.127	72.852	0.147	8.95
108.50	5.65 5.56	7.400	72.998	0.126	9.07
119.90	6.18	8.280	73.128	0.096	9.18
126.22	6.68	8.689	73 330	0.090	9.22
132.78	6.48	9.127	73.450	0.106	8.07
139.07	0.07	9.333	73.568	0.107	7.57
152.20	6.42	10.32	73.686	0.115	7.22
156.92	6.14	10.58	73.810	0.118	0.99
163.35	6.67	10.91	74.060	0.120	6.75
169.87	6.34	11.24	74.192	0.123	6.63
170.70	6.87	11.57	74.320	0.124	6.56
190.98	7.17	12.23	74.448	0.125	6.52
198.08	6.87	12.50	74.581	0.120	0.44 6 30
205.90	6.55	12.81	74.837	0.128	6.35
213.03	7.57	13.01*	74.967	0.129 •	6.30
220.38 227.40	5.84	13.51*	75.097	0.130	6.26
236.39	6.68	13.79	15.228	0.150	0.24
243.24	6.87	14.01	51	DIES VI	r
251.28	0.03	14.19		SKIES VI	1
266.19	7.47	14.53	71.530	0.182	8.02
274.30	7.45	14.76	71.711	0.182	8.07
282.40	8.70	14.95	72.087	0.179	8.33
290.31	8.33	15.13	72.243	0.100	8.48
270.25	0.25	15.57	72.352	0.100	8.53
5	SERIES IV	,	72.460	0.100	8.59
11.14	0.52	0.044	72.683	0.099	8.76
11.88	0.98	0.050	72.787	0.098	8.90
13.76	1.40	0.072	72.891	0.097	8.98
15.42	1.71	0.102	72.994	0.097	9.07
19.73	2.23	0.222	73.201	0.090	9.18
22.09	2.26	0.327	73.302	0.098	8.99
24.74	2.76	0.484	73.407	0.105	8.20
27.54	2.84	0.687			T.
33.21	2.92	1.204	SE	KIES VII	L I
36.25	3.08	1.533	81.25	2.67	5.956
39.37	3.18	1.895	83.84	2.56	6.029
42.67	3.35	2.309	216.10	7.26	13.18
40.33 50.85	4.30	2.047	230.55	6.73	13.42
59.27	13.54	4.894	237.50	6.51	13.86
74.95	17.41	6.653	299.99	6.50	15.30
			1		

* Point unreliable because of bad vacuum conditions,

mentally the value of the correction for every filling of the calorimeter. In the measurements on NiF₂ the correction was positive and its maximum value amounted to 1.4 percent at 298°K. The correction is proportional to the thermal conductance between the calorimeter and shield and decreases rapidly as the temperature is lowered. Thus in the measurements on NiF2 it was down to 0.2 percent at 200°K and rapidly became negligible at lower temperatures. After the completion of the measurements on NiF₂ it was discovered that in the filling of the thermometer case with helium some air had inadvertently been introduced. Upon refilling the case with pure helium the thermal conductance between the wire and the case increased by a factor of about three. This brought the thermometer in better contact with the outside of the calorimeter and in the measurements on FeF_2 , CoF_2 , and ZnF_2 to be described in later papers the correction discussed above was negative in sign and considerably smaller in magnitude than was the case for NiF_2 .

PREPARATION OF SAMPLE

Hydrated nickel fluoride was prepared following the general procedure of Kurtenacker, Finger, and Hey.14 Nickel carbonate was precipitated by adding a solution of sodium bicarbonate to one prepared by dissolving commercial "Special low cobalt" NiSO4.6H2O in distilled water. An excess of the nickel sulfate solution was used in order to minimize the precipitation of other metallic carbonates. The precipitated carbonate, after filtering and washing, was added to an aqueous solution of HF contained in a plastic dish. NiF₂·4H₂O crystallized from this solution and a larger yield was obtained by the addition of ethanol. The filtered $NiF_2 \cdot 4H_2O$ was dried in an oven at 120°C. The resulting product corresponded approximately to the monohydrate. The remaining water was removed by heating the material in a nickel boat contained in a nickel tube through which commercial anhydrous hydrogen fluoride was passed. The water came off at a temperature of 350-400°C. In order to insure complete dehydration and to obtain larger crystallites of NiF₂ the temperature of the furnace was increased gradually to 900°C and kept at this temperature for about an hour with HF passing over the sample. The NiF_2 so prepared was a light greenish-yellow color.

Microscopic examination showed that the sample consisted of crystallites with a range of 0.005 to 0.01 mm in diameter. The individual crystallites showed extinctions when rotated between crossed Nicols, indicating that they were single crystals of an optically anisotropic material such as NiF₂. The crystal size observed was sufficiently large so that surface effects would be negligible in the thermal properties. In a spectrochemical analysis of the NiF₂ the only metallic

¹⁴ Kurtenacker, Finger, and Hey, Z. anorg. Chem. 211, 83 (1933).

impurities found were, in weight percent: Cu, 0.005; Co, 0.004; Fe, 0.003; Mn, 0.001. X-ray diffraction photographs¹ showed no lines not attributable to NiF₂. The sintered NiF₂ was extremely inert to attack by chemical reagents and we did not find a satisfactory method of dissolving it so as to make an accurate analytical determination of the nickel content of the sample. It was found that if the NiF₂ was heated with ground silica the fluoride was converted to an oxide which could be dissolved in HCl, and the nickel then determined gravimetrically by a dimethylglyoxime precipitation. Four such determinations gave results ranging from 60.9 to 63.1 percent of nickel in the original sample, compared to 60.70 percent calculated from the formula NiF₂.

EXPERIMENTAL RESULTS

The observed heat capacity data are given, in chronological order, in Table I. The sample of NiF₂ weighed 123.97 g in vacuo (1.2822 moles). The defined calorie used is equal to 4.1840 absolute joules. The heat capacities listed in Table I are values of $\Delta H/\Delta T$ (*H* is the enthalpy) and are equal to the true differential heat capacity, C_p , only if the correction for curvature is negligible. Actually the correction for curvature exceeds the experimental error only in the points in the vicinity of the anomaly near 73°K. Also listed in Table I are values of the approximate temperature rise of each measurement. The temperature given for each point is the arithmetic mean of the initial and final temperatures.

Series I comprises several exploratory measurements after the initial cooling of the calorimeter to liquid nitrogen temperatures. The calorimeter was then cooled to 51° K and the data of series II taken. The calorimeter remained at about 85° for three days and then the measurements of Series III, extending to room temperature, were made.

The three points in this series, at temperatures between 210 and 230°K and marked by an asterisk in Table I, are below a smooth curve. The thermal drift during these points was abnormally large, caused probably by poor vacuum from the evaporation of condensed CO₂. Under such conditions the precision of the measurements is poor and these points should be given little weight. The region of temperature between 210 and 240°K was covered, with good vacuum conditions, by points listed under Series VIII. Two days after the completion of Series III the calorimeter was cooled to liquid hydrogen temperatures and the data of Series IV obtained. The last two points in this series are very long runs designed to obtain accurate values for the change in enthalpy through the region of anomalous heat capacity. The calorimeter then stood for one day at 83°K, was cooled to 49.8°K, and warmed overnight to 50.5°K where the measurements of Series V began. A point in this series at 72.2°K has been dis-



FIG. 1. Heat capacity of NiF_2 in the anomalous region.

carded because of uncertainty in the energy input readings.

In order to define more closely the shape of the curve in the anomalous region heat capacity measurements with a temperature rise of about one-tenth degree were taken in Series VI and VII. Because of the small temperature rise these measurements are less accurate than the usual ones. We estimate that they are reliable to about 0.5 percent. Although the error in the absolute temperature calculated from the resistance thermometer may be several hundredths of a degree, small differences in temperature are known to better than one thousandth of a degree. In Table I we have listed the mean temperature of the measurements of Series VI and VII to the nearest 0.001° in order to show the variation of heat capacity with temperature. Two days after the completion of Series V, the calorimeter, which had remained at 85°K, was cooled to 72.5°K and the measurements of Series VI were taken. Seven days later the temperature of the calorimeter had risen to 120°K. It was cooled to 71.4°K and Series VII begun. There is no evidence from any of the measurements of dependence of the observed heat capacity on the thermal history of the sample and the points from all series are consistent within the expected error. In the neighborhood of the maximum in heat capacity there was no evidence of slowness in the attainment of thermal equilibrium.

THE ANOMALY IN HEAT CAPACITY

The heat capacity data between 60 and 85°K are plotted in Fig. 1. Points in which the temperature rise was so large that the mean heat capacity, $\Delta H/\Delta T$, deviates appreciably from the heat capacity at the mean temperature have been omitted. The observed mean heat capacity of such points agrees within 0.2 percent with that obtained from integration of the smooth curve. The anomaly in heat capacity has the lambda shape characteristic of processes where cooperative ordering is taking place. The peak in heat

TABLE II. Thermodynamic properties of NiF₂.

				$F^0 - H_{0^0}$
Т	C_p^0 cal deg ⁻¹	S⁰ cal deg⁻ı	$H^0 - H_{0^0}$	T cal deg ⁻¹
°K	mole ⁻¹	mole ⁻¹	cal mole ⁻¹	mole ⁻¹
15	0.094	0.050	0.44	0.020
20	0.232	0.093	1.21	0.033
25	0.500	0.171	2.98	0.052
30	0.891	0.295	6.42	0.081
35	1.393	0.469	12.10	0.124
40	1.969	0.692	20.47	0.180
45	2.626	0.961	31.92	0.252
50	3.354	1.275	46.87	0.338
55	4.127	1.631	65.53	0.439
60	5.013	2.027	88.34	0.555
65	6.025	2.467	115.8	0.685
70	7.36	2.958	149.0	0.829
73.22	9.23	3.320	175.2	0.927
75	0.28	3.489	18/.0	0.980
80	5.943	3.8/8	217.0	1.100
85	0.070	4.241	241.0	1.320
90	0.310	4.393	210.1	1.490
100	0.925	5.290	117 A	2 1 8 7
110	9 286	6.672	406.8	2.107
120	8.200	7 362	583.0	2.332
140	0.545	8 040	675 7	3 222
150	10 10	8 731	774.7	3 567
160	10.19	9 407	879.4	3.911
170	11 25	10 073	989.3	4.254
180	11.72	10.729	1104.2	4.595
190	12.16	11.375	1223.6	4.935
200	12.57	12.009	1347.3	5.273
210	12.96	12.632	1474.9	5.609
220	13.31	13.243	1606.3	5.942
230	13.61	13.841	1740.9	6.272
240	13.90	14.427	1878.5	6.600
250	14.16	15.000	2018.8	6.924
260	14.41	15.560	2161.7	7.246
270	14.65	16.109	2307.0	7.564
280	14.89	16.646	2454.7	7.879
290	15.12	17.172	2604.7	8.190
300	15.36	17.689	2757.1	8.498
273.16	14.72	16.28	2353	7.66
298.16	15.31	17.59	2729	8.44
2,0.10		± 0.04	±5	± 0.02

capacity is narrower and appears somewhat sharper than that observed⁸ in MnF₂. The question as to whether the curve near the maximum is continuous with continuous derivative, or cusped, cannot be unambiguously answered from the data. Because of the finite temperature increment in each heat capacity measurement a cusped curve would appear smoothed out. Any further reduction in the temperature increment below the approximately 0.1° we used would decrease the precision and not assist in deciding the shape of the curve. It appears from a large scale plot of the data in the immediate neighborhood of the maximum that, taking into account the finite resolution and precision of the points, the data are better represented by a smooth curve than by a cusped one. Undoubtedly there is a large change from positive to negative slope in the heat capacity-temperature curve between 73.15 and 73.3°K. The maximum heat capacity is 9.23 cal mole⁻¹ deg⁻¹ at a temperature of $73.22 \pm 0.05^{\circ}$ K.

The heat capacity anomaly is evidently connected with the ordering of the atomic magnetic moments. From an extrapolation of magnetic structure factors obtained in neutron diffraction experiments Erikson⁵ concluded that the long-range order disappears at 83°K. The extrapolation was based on the assumption that the magnetization of each sublattice is that calculated from the Van Vleck theory.7 It seems probable from the narrowness of the heat capacity anomaly that the actual sublattice magnetization near the Curie temperature is varying much more rapidly with temperature than is given by the Van Vleck theory and a reasonable extrapolation of Erickson's data to a temperature of 73.22°K may be made. Matarrese and Stout⁴^c found that the temperature below which an anomalous behavior in the magnetic anisotropy of a single crystal of NiF₂ appeared was close to the 73.22°K of the maximum in heat capacity.

THERMODYNAMIC PROPERTIES OF NiF2

Values of the heat capacity, entropy, and the enthalpy and free energy functions of NiF₂ at selected temperatures are listed in Table II. The values of C_p are differential heat capacities and in drawing the smooth curves the experimental points were corrected for curvature. It was found that the experimental values of the heat capacity at the lowest temperatures were varying much more slowly with temperature than predicted by a Debye function. Since much of this heat capacity arises from the magnetic properties of NiF₂, which are imperfectly understood theoretically, the extrapolation to 0°K was made by an arbitrary extension, on a plot of C_p/T versus T, of a reasonable curve to the absolute zero. The extrapolated contribution to the entropy below 11°K is only 0.03 cal deg⁻¹ mole⁻¹. The accuracy of the smoothed heat capacity data is estimated as 3 percent at 15°K, 1 percent at 20°K and 0.2 percent at 40°K. In the neighborhood of the maximum the smooth curve may be in error by 0.5 percent. From 75°K to 200°K the accuracy is about 0.2 percent and, because of the increased heat leak and uncertainty in the corrections for temperature gradients in the calorimeter, rises to about 0.5 percent at 300°K. Although the accuracy of the functions S^0 , $H^0 - H_0^0$ and $-(F^0 - H_0^0)/T$ is about 0.2 percent above 100°K the numbers in Table II are given to a higher precision than this so that they will be internally consistent.

The values of entropy and free energy in Table II do not include the contributions arising from nuclear spin randomness or isotope mixing. They do, however, include that arising from randomness in the orientation of electronic spins. The magnetic susceptibility ^{2,40} and neutron diffraction⁵ data show that the spin system is essentially completely ordered at 12°K and calculations to be presented in a later paper show that the anomalous heat capacity is consistent with an entropy loss of R ln3 per mole of NiF_2 . The values of the thermodynamic quantities listed in Table II are therefore the correct ones to be used in calculations of chemical equilibria.

With the thermodynamic functions calculated from the low-temperature heat capacity measurement it is possible to obtain from equilibrium data more accurate values for the heats of chemical reactions involving NiF_2 than may be calculated from the temperature coefficient of the equilibrium constant. As an example we shall consider the reaction $NiF_2+H_2=Ni+2HF$. Equilibrium constants have been measured over the range 573-773°K by Jellinek and Rudat.¹⁵ Values of the free energy and entropy functions are given for HF by Cole, Farber, and Elverum,¹⁶ for Ni by Busey and Giauque¹⁷ and Kelley,¹⁸ and those for H₂ are taken from the summary of Wagman et al.¹⁹ An extrapolation of the observed heat capacity data on NiF2 was made, passing through the value 17.7 cal deg⁻¹ mole⁻¹ at 500°K and 19.1 at 800°K, and values of the free energy and enthalpy functions were calculated from this curve. From the x-ray examination¹ of single crystals grown from the melt it is likely that no phase changes occur in NiF_2 in this region of temperature. Although the extrapolation of the heat capacity is uncertain, this uncertainty does not introduce a large error in the free energy function. Thus if one makes the extreme assumption that the heat capacity of NiF₂ remains constant at all temperatures above 300°K the values of $-(F^0-H_0^0)/T$ are below those calculated from our extrapolated curve by 0.10 and 0.54 cal deg⁻¹ mole⁻¹ at 500 and 773°K, respectively. Table III summarizes the calculation of the values of ΔH_0^0 . In calculating the

TABLE III. $\Delta H_{0^{0}}$ for reaction NiF₂+H₂=Ni+2HF. Equilibrium data of Jellinek and Rudat (see text).

T,°K	$\log\left(P^{2}_{\rm HF}/P_{\rm H2}\right)$	$\Delta F^0/T$ cal deg ⁻¹	$\Delta (F^0 - H_0^0)/T$ cal deg ⁻¹	∆H₀⁰ kcal
573	-2.48	11.35	-40.06	29.46
673	-0.86	3.94	- 39.91	29.51
723	-0.26	1.19	-39.82	29.65
773	0.32	-1.46	-39.73	29.58
			Mean	29.50

mean value, the datum at 573°K has been given half weight. We estimate the error, arising from uncertainties in the extrapolation of the heat capacity of NiF_2 and from the scatter of the values of ΔH_0^0 , to be 0.20 kcal. The values of ΔH^0 at other temperatures may be calculated from the tables of $H^0 - H_0^0$. For the reaction $NiF_2 + H_2 = Ni + 2HF$ we obtain $\Delta H_0^0 = 29.56 \pm 0.20$ kcal and $\Delta H^0 = 30.06 \pm 0.20$ kcal at $T = 298.16^{\circ}$ K. From the temperature coefficient of the equilibrium constant Jellinek and Rudat calculated a value of $\Delta H^0 = 29.6$ kcal at T = 673 °K. Using our values of the extrapolated enthalpy of NiF₂ this becomes $\Delta H^0 = 30.7$ kcal at T = 298.16. This value is considerably less accurate than the 30.06 ± 0.20 kcal we have calculated from the same equilibrium data by using low-temperature heat capacity data and the third law of thermodynamics, both because of the errors inherent in determining the temperature coefficient of an equilibrium constant over a limited temperature range and because the possible errors in the enthalpy function of NiF₂, arising from uncertainty in the extrapolation of the heat capacity, are about four times those in the free energy function.

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