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Thermodynamic Properties of $NiBr_2$ and $NiSO_4$ From 10 to 1,200 K

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16. Abstracts
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Thermodynamic Properties of $NiBr_2$ and $NiSO_4$ From 10 to 1,200 K

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UNITED STATES DEPARTMENT OF THE INTERIOR
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BUREAU OF MINES

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THERMODYNAMIC PROPERTIES OF $NiBr_2$ AND $NiSO_4$ FROM 10 TO 1,200 K

by

J. M. Stuve,[1] M. J. Ferrante,[1] and H. C. Ko[1]

ABSTRACT

The present Bureau of Mines investigation measured low-temperature heat capacities of $NiBr_2$ (8 to 302 K) and $NiSO_4$ (9 to 70 K) by adiabatic calorimetry. The standard entropies (S°, 298.15 K) of $NiBr_2$ and $NiSO_4$ were calculated as 29.26 ± 0.06 cal/deg mole and 24.21 ± 0.04 cal/deg mole, respectively. (1 cal = 4.1840 joules.) Heat-of-solution measurements of anhydrous $NiBr_2$ were used to determine its enthalpy of formation (ΔHf°, 298.15 K) as -50.64 ± 0.31 kcal/mole. High-temperature enthalpies of $NiBr_2$ and $NiSO_4$ were measured by drop calorimetry to 1,150 K and 1,002 K, respectively. Enthalpies, heat capacities, and related formation functions are tabulated to 1,200 K.

INTRODUCTION

This investigation was undertaken to support the Bureau of Mines effort to provide alternative methods for extracting nickel from low-grade domestic ore deposits. The accurate determination of absolute entropies, formation enthalpies, and high-temperature enthalpies of $NiBr_2$ and $NiSO_4$ provides key parameters for evaluation of metallurgy-related equilibria.

The low-temperature heat capacity of $NiSO_4$ had been measured to near 50 K by Weller (12).[2] The present investigation of $NiSO_4$ extended this data below the range of Weller's apparatus to ascertain the extrapolated portion of entropy. A large heat-capacity anomaly was observed near 36 K. In the course of measuring the heat capacity of $NiBr_2$, no sharp peak was found; however, a slight "bump" in the data around 46 K was detected.

The enthalpy of formation of $NiBr_2$ was determined by precision solution calorimetry using 4.36 molal HCl solutions. Prior measurements by Adami and King (1) gave the enthalpy of $NiSO_4$ formation at 298.15 K.

High-temperature enthalpy measurements were made to 1,150 K with $NiBr_2$ and to 1,002 K for $NiSO_4$. No unusual transition or thermal anomalies were

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

measurements, the sample was sealed in the calorimeter vessel with a partial atmosphere of helium gas to promote good thermal conductivity.

The heat capacities of crystalline $NiBr_2$(c) were measured over the temperature range 7.8 to 303 K. The experimental heat-capacity data are given in table 1 and illustrated in figure 1. Slight excess heat capacity was noted in the range 40 to 55 K.

TABLE 1. - Experimental heat capacities of $NiBr_2$(c)

Temperature, K	Cp, cal/deg mole	Temperature, K	Cp, cal/deg mole
7.89	0.230	57.75	8.666
8.67	.282	63.48	9.533
9.68	.359	69.02	10.323
10.84	.456	73.12	10.861
12.14	.564	78.35	11.495
13.63	.687	84.44	12.159
15.25	.826	91.86	12.871
17.03	1.000	100.21	13.563
18.79	1.188	109.38	14.181
20.55	1.402	119.01	14.737
22.48	1.666	128.86	15.209
24.94	2.050	139.38	15.621
27.62	2.514	150.05	15.981
30.30	3.035	160.92	16.281
32.95	3.605	172.32	16.548
35.69	4.232	183.51	16.781
38.76	5.016	195.28	16.975
41.97	5.930	207.70	17.171
42.93	6.231	220.01	17.335
44.13	6.598	232.22	17.484
44.91	6.804	244.36	17.567
46.50	7.120	256.44	17.711
48.11	7.334	267.72	17.787
48.47	7.364	278.96	17.867
49.11	7.447	290.97	17.965
52.41	7.861	302.95	18.054
55.00	8.222		

Experimental data for $NiSO_4$(c) are listed in table 2 and presented graphically in figure 2. The data points above 77 K were taken from Weller (12). A sharp thermal transition was observed in the heat capacity at 35.5 K with the posttransition curve merging with the normal lattice heat-capacity curve at about 50 K.

TABLE 2. - Experimental heat capacities of $NiSO_4$(c)

Temperature, K	Cp, cal/deg mole	Temperature, K	Cp, cal/deg mole
SERIES 1		SERIES 2	
9.69	0.136	30.51	3.207
10.09	.153	31.38	3.468
11.40	.224	32.29	3.783
12.83	.326	33.12	4.108
14.14	.449	33.82	4.621
15.75	.645	34.39	4.756
17.77	.861	34.99	5.214
19.74	1.121	35.63	5.403
21.65	1.397	36.36	3.338
23.68	1.729	37.27	2.662
26.40	2.237	38.23	2.510
29.47	2.935	39.18	2.444
32.56	3.923	54.29	3.469
36.31	3.815	58.33	3.983
41.30	2.460	62.90	4.568
46.92	2.727	69.59	5.372
51.99	3.197		

The experimental data were computer-fitted with polynomial functions (5) to obtain smooth values of heat capacity at even temperature intervals. The resulting values of heat capacity (Cp), as well as entropy (S°), Gibbs free energy function $(G°-H_0°)/T$, and enthalpy relative to 0 K $(H°-H_0°)$, are listed in tables 3 and 4. In the case of $NiSO_4$, Weller's data (12) were used to complete the table to 300 K. Temperatures listed are based on the International Practical Temperature Scale of 1968, according to NBS calibrations of the platinum resistance thermometer. Uncertainties in the measured heat capacities vary with sample temperature. As an approximate guide, these uncertainties are estimated as follows: 5 to 15 K, ±5 pct; 15 to 50 K, ±0.2 pct; 50 to 300 K, ±0.1 pct.

TABLE 4. - Low-temperature thermodynamic properties of $NiSO_4$(c)

Temperature, K	Cal/deg mole			Cal/mole, $H°-H°_0$
	Cp°	S°	$-(G°-H°_0)/T$	
5	0.018	0.008	0.001	0.033
10	.150	.049	.012	.368
15	.538	.172	.042	1.944
20	1.157	.407	.102	6.100
25	1.966	.748	.195	13.824
30	3.069	1.197	.323	26.227
35	5.200	1.798	.489	45.822
40	2.450	2.240	.685	62.22
45	2.624	2.535	.858	75.45
50	3.015	2.830	1.056	88.69
55	3.523	3.141	1.232	105.00
60	4.131	3.472	1.404	124.09
65	4.846	3.831	1.577	146.52
70	5.440	4.211	1.751	172.18
80	6.665	5.018	2.109	232.73
90	7.862	5.872	2.479	305.39
100	9.018	6.761	2.863	389.83
110	10.124	7.673	3.259	485.59
120	11.177	8.599	3.665	592.1
130	12.176	9.534	4.080	709.0
140	13.122	10.471	4.503	835.5
150	14.015	11.407	4.932	971.2
160	14.861	12.339	5.367	1,115.6
170	15.66	13.264	5.803	1,268.3
180	16.42	14.181	6.244	1,428.7
190	17.15	15.09	6.687	1,596.6
200	17.84	15.99	7.132	1,771.6
210	18.51	16.87	7.569	1,953.3
220	19.14	17.75	8.015	2,141.6
230	19.76	18.61	8.453	2,336.1
240	20.35	19.47	8.900	2,536.7
250	20.92	20.31	9.338	2,743.0
260	21.46	21.14	9.775	2,954.9
270	21.98	21.96	10.211	3,172.1
273.15	22.13	22.22	10.346	3,241.6
280	22.47	22.77	10.648	3,394.3
290	22.95	23.56	11.072	3,621.4
298.15	23.33	24.21	11.431	3,810.0
300	23.42	24.35	11.506	3,853.3

TABLE 6. - Auxiliary reactions for $NiBr_2$(c) at 298.15 K

Reaction	ΔH, kcal	Uncertainty, kcal	Reference[1]
(9) 0.5 H_2(g) + 0.5 Cl_2(g) + 12.731 H_2O(l) = HCl·12.731 H_2O(l)...........................	-38.820	0.040	10
(10) Na(c) + 0.5 Br_2(l) = NaBr(c)..................	-86.380	.100	3
(11) Ni(c) + S(rh) + 2 O_2(g) = $NiSO_4$(c)............	-208.63	.100	1, 11
(12) Na(c) + 0.5 Cl_2(g) = NaCl(c)..................	-98.260	.080	3
(13) H_2(g) + 2 O_2(g) + 6H_2O(l) + S(rh) = H_2SO_4·6H_2O(l)..............................	-208.944	.100	10
(14) Ni(c) + Br_2(l) = $NiBr_2$(c).....................	-50.64	.31	-
$\Delta H_{14} = \Delta H_8 + 2\Delta H_9 + 2\Delta H_{10} + \Delta H_{11} - 2\Delta H_{12} - \Delta H_{13}$			

[1]References are given at end of report.

HIGH-TEMPERATURE ENTHALPY

The enthalpies of $NiBr_2$ and $NiSO_4$ relative to 298.15 K were measured using a copper-block drop calorimeter similar to one described by Douglas and King (2). The samples of $NiBr_2$ and $NiSO_4$ were approximately 0.054 g-mole and 0.041 g-mole, respectively. They were encapsulated in previously calibrated platinum-rhodium containers and back-filled with a helium atmosphere.

The experimental enthalpy values for $NiBr_2$ and $NiSO_4$ are tabulated in table 7 and plotted in figures 3 and 4. The experimental enthalpies were fitted with polynomial functions to calculate the enthalpies at even temperature values (smooth values). These smooth values are the basis of the lined curve through the experimental points in figures 3 and 4. The computed enthalpy values and related thermodynamic functions are listed in tables 8 through 10.

TABLE 9. - Thermodynamic properties of $NiSO_4(c)$

[Formation: $Ni(c) + 2S(r,l) + 2\ O_2(g) = NiSO_4(c)$]

Temperature, K	Cal/deg mole			Kcal/mole			Log Kf
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
298.15........	23.33	24.21	24.21	0	-208.63	-182.22	133.573
300...........	23.42	24.35	24.22	.043	-208.64	-182.06	132.632
368.5[1]........	26.22	29.51	24.72	1.765	-208.71	-175.98	104.358
368.5.........	26.22	29.51	24.72	1.765	-208.81	-175.98	104.358
388.4[2]........	27.03	30.91	25.00	2.293	-208.81	-174.21	98.038
388.4.........	27.03	30.91	25.00	2.293	-209.22	-174.21	98.038
400...........	27.51	31.71	25.19	2.611	-209.24	-173.16	94.612
500...........	30.05	38.14	27.14	5.496	-209.46	-164.11	71.733
600...........	31.91	43.79	29.46	8.598	-209.51	-155.04	56.472
631[3]..........	32.36	45.41	30.20	9.596	-209.51	-152.22	52.722
700...........	33.37	48.82	31.86	11.870	-209.39	-145.95	45.569
718.8[4]........	33.58	49.66	32.29	12.465	-209.35	-144.34	43.947

[1]Phase change S (rhombic) = S (monoclinic).
[2]Melting point of sulfur.
[3]Curie temperature of nickel.
[4]Boiling point of sulfur.

TABLE 10. - High-temperature formation of $NiSO_4(c)$, $S_2(g)$ reference

[Formation: $Ni(c) + 0.5S_2(g) + 2\ O_2(g) = NiSO_4(c)$]

Temperature, K	Cal/deg mole			Kcal/mole			Log Kf
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
298.15......	23.33	24.21	24.21	0	-223.97	-191.71	140.529
300.........	23.42	24.35	24.22	.043	-223.98	-191.51	139.518
400.........	27.51	31.71	25.19	2.611	-223.88	-180.70	98.729
500.........	30.05	38.14	27.14	5.496	-223.57	-169.93	74.278
600.........	31.91	43.79	29.46	8.598	-223.19	-159.24	58.005
631[1]........	32.36	45.40	30.20	9.596	-223.07	-155.94	54.011
700.........	33.37	48.82	31.86	11.870	-222.70	-148.61	46.399
800.........	34.57	53.36	34.29	15.265	-222.08	-138.09	37.723
900.........	35.56	57.49	36.63	18.770	-221.39	-127.62	30.991
1,000.........	36.38	61.28	38.91	22.370	-220.64	-117.24	25.624
1,100.........	37.03	64.78	41.11	26.040	-219.87	-106.94	21.246
1,200.........	37.53	68.02	43.21	29.770	-219.08	-96.70	17.612

[1]Curie temperature of nickel.

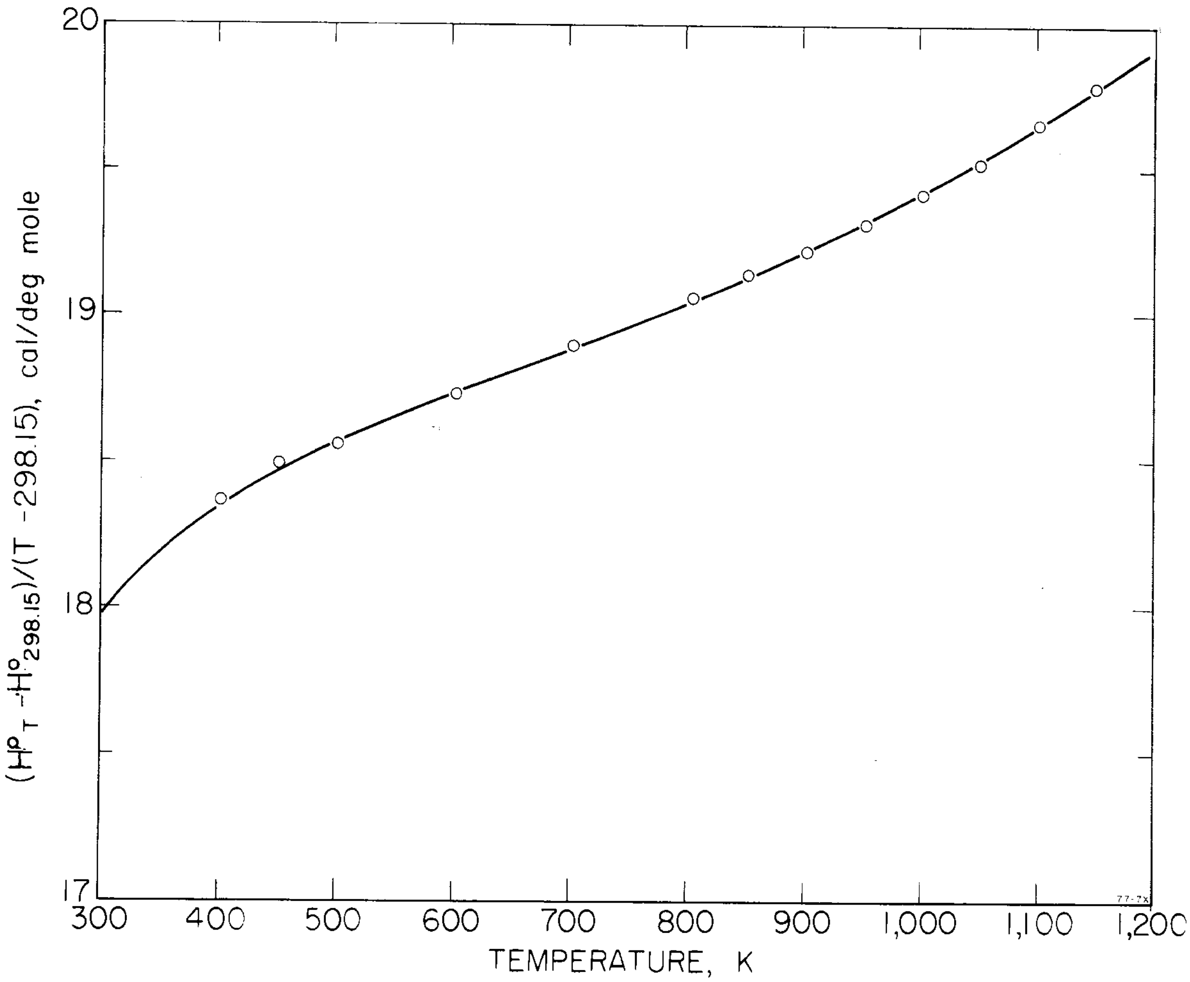

FIGURE 4. - High-temperature enthalpy of $NiSO_4$.

SUMMARY OF RESULTS

The results of the low-temperature formation enthalpy and high-temperature measurements from the previous sections are summarized in tables 8 through 10. The last three columns list the enthalpy of formation (ΔHf°), Gibbs energy of formation (ΔGf°), and the log (base 10) of the formation equilibrium constant (log Kf). Values given beyond the range of experimental measurements are based on reasonable extrapolation of experimental data.

The standard entropy of nickel and enthalpy data above 298 K were taken from Hultgren (4). Corresponding data for Br_2, S, O_2, and S_2 were those given in the JANAF Thermochemical Tables (3). It should be noted that formation data above the boiling point of sulfur (717.8 K) are referenced to $S_2(g)$. This was convenient because there is no single gaseous species in thermal equilibrium with liquid sulfur.

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