[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Nickel from 15 to 300°K. Entropy and Free Energy Functions[1]

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

RECEIVED FEBRUARY 2, 1952

The heat capacity of nickel has been measured from 15 to 300°K. The entropy, heat content and free energy functions have been calculated.

The work reported here was done because the free energy function for nickel was needed in connection with an equilibrium study of the reduction of nickel chloride by hydrogen at temperatures up to some 700°K.

A sample of very pure nickel was prepared through the courtesy of the research laboratory of the International Nickel Company, which supplied the following analysis:

C	Al	B	Ca	Co	Cu	Fe	Pb
0.014%	VST	VST	VST	0.0018%	0.0009%	VST	NF
Mg	Sn	As	Ag	Na	V	Zn	Si
VST	NF	NF	NF	NF	NF	NF	VST

NF = none found. VST = very slight trace.

The carbon was determined by combustion and the cobalt and copper by wet analysis. The other elements were evaluated by spectrographic comparison. By this method copper was given as VST which apparently can be taken as of the order of 0.001%. The sample had been prepared in the form of a cylinder 4.2 cm. diam. × 10.8 cm. long. The cast cylinder had been annealed at 900° for 2 hours in an atmosphere of hydrogen. Before the nickel was placed in the calorimeter the sample was heated inductively *in vacuo* to remove any hydrogen which may have dissolved in the nickel. It was held between 1000 and 1100° with a vacuum down to 2×10^{-5} mm. for 5 hr. and between 1100 and 1200° and a vacuum down to 8×10^{-6} mm. for an additional 5 hr. It was cooled *in vacuo* to 800° in one hour and then slowly to 100° over a period of 17 hr. before removal. The sample weighed 1309.79 g. *in vacuo*. The atomic weight was taken as 58.69.

The measurements were made in the calorimeter described by Giauque and Meads[2] except that a standard copper–constantan thermocouple with the laboratory designation W-26 was used. The thermocouple had been compared with a helium gas thermometer and was checked against the following fixed points at the conclusion of the present measurements: triple point (13.92°K.) and boiling point (20.36°K.) of hydrogen, and the triple point of nitrogen (63.15°K.). One calorie was taken as 4.1840 absolute joules.

The observed data are given in Table I.

The heat capacity of nickel has been measured by Rodebush and Michalek[3] from 67 to 106°K. and from 196 to 203°K.; by Simon and Ruhemann[4] from 71 to 83°K.; by Eucken and Werth[5] from 15 to 204°K.; by Bronson and Wilson[6] from 203 to 303°K. and by Aoyama and Kanda[7] from 80 to 273°K.

TABLE I

HEAT CAPACITY OF NICKEL

°C. = 273.16°K.; cal. deg.$^{-1}$ (g. atom)$^{-1}$; at. wt. = 58.69

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		82.22	2.534	196.03	5.322
12.95	0.036	88.52	2.800	204.43	5.423
14.68	.037	95.13	3.067	212.96	5.513
16.71	.052	102.07	3.335	221.33	5.585
19.46	.075	109.01	3.580	229.59	5.655
22.78	.107	116.23	3.797	238.59	5.729
26.37	.159	123.62	3.996	247.96	5.820
30.14	.236	131.77	4.205	Series II	
33.83	.332	139.64	4.395	238.75	5.732
37.86	.458	147.50	4.565	247.95	5.818
42.93	.647	155.38	4.722	256.73	5.890
48.93	.902	163.33	4.857	265.59	5.960
54.89	1.199	171.37	4.989	274.81	6.031
62.12	1.552	179.48	5.112	284.34	6.101
69.74	1.932	187.68	5.221	302.98	6.295
75.91	2.236			293.99	6.198

The results of Rodebush and Michalek are about 1.3% high in the range 67 to 106°K. and about 2.8% high near 200°K. The few measurements of Simon and Ruhemann are about 3% above the present results. The data of Eucken and Werth average about 2% low in the range 15 to 35°K., 1% high from 35 to 80°K., 0.4% low from 80 to 130°K. and 0.4% high from 130 to 200°K. The results of Bronson and Wilson are 0.4% high from 203 to 273°K. and 0.25% low from 273 to 303°K. The data of Aoyama and Kanda average about 1% high over the range 80 to 273°K. It is difficult to say how many of the above differences are due to impure samples and unknown physical state. Rodebush and Michalek used 99+% Ni. Eucken and Wilson had 0.5% Mn in their sample. Bronson and Wilson used nickel with 0.03% Cu, 0.13% Fe, 0.10% Si and 0.03% C. Aoyama and Kanda used very pure nickel.

Keesom and Clark[8] have measured the heat capacity of nickel from 1 to 20°K. They give the equation

$$C = 6.594 \times 10^{-6} T^3 + 0.001744 T$$

over the above range. Their sample contained 99.81% Ni, 0.017% Cu, 0.083% Fe, 0.037% Mg and 0.04% C.

Clusius and Goldmann[9] have covered the range 10 to 26°K. No analysis of their sample is given.

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

(2) W. F. Giauque and P. F. Meads, THIS JOURNAL, **63**, 1897 (1941).

(3) W. H. Rodebush and J. C. Michalek, *ibid.*, **47**, 2117 (1925).

(4) F. Simon and M. Ruhemann, *Z. physik. Chem.*, **129**, 321 (1927).

(5) A. Eucken and H. Werth, *Z. anorg. allgem. Chem.*, **188**, 152 (1930).

(6) H. L. Bronson and A. J. C. Wilson, *Can. J. Research*, **14A**, 181 (1936).

(7) S. Aoyama and E. Kanda, *J. Chem. Soc. Japan*, **62**, 312 (1941).

(8) W. H. Keesom and C. W. Clark, *Physica*, **2**, 513 (1935).

(9) K. Clusius and J. Goldmann, *Z. physik. Chem.*, **31**, 256 (1936).

The results of Clusius and Goldmann agree well with those of Keesom and Clark, and join well with the results of the present research. The results of Keesom and Clark made extrapolation necessary only below 1°K. in obtaining the entropy.

The thermodynamic properties of nickel calculated from the present results are given in Table II.

Calculations were extended to 800°K. on the basis of available data; however, the increments above 298.16°K. were in substantial agreement with calculations of Kelley,[10] who has summarized all available results as increments above 298.16°. To combine the results

$$S = 7.14 + (S - S_{298.16})_{\text{Kelley}}$$

$$\frac{H^\circ - H_0^\circ}{T} = \frac{3.837 \times 298.16 + (H_T - H_{298.16})_{\text{Kelley}}}{T}$$

and

$$\frac{F^\circ - H_0^\circ}{T} = \frac{H^\circ - H_0^\circ}{T} - S$$

TABLE II

THERMODYNAMIC PROPERTIES OF NICKEL

T, °K.	C_p	S	$\frac{H^\circ - H_0^\circ}{T}$	$-\frac{(F^\circ - H_0^\circ)}{T}$
15	0.043	0.033	0.018	0.015
20	.081	.050	.029	.021
25	.142	.074	.045	.029
30	.234	.107	.068	.039
35	.367	.153	.101	.052
40	.534	.213	.145	.068
45	.732	.287	.199	.088
50	.956	.375	.263	.112
60	1.448	.592	.418	.174
70	1.953	.853	.601	.252
80	2.433	1.145	.800	.345
90	2.868	1.456	1.005	.451
100	3.258	1.778	1.211	.568
110	3.605	2.105	1.413	.692
120	3.903	2.432	1.608	.824
130	4.164	2.755	1.795	.960
140	4.401	3.073	1.974	1.099
150	4.614	3.384	2.143	1.241
160	4.802	3.688	2.304	1.384
170	4.969	3.984	2.455	1.529
180	5.118	4.272	2.599	1.673
190	5.250	4.552	2.735	1.817
200	5.370	4.824	2.863	1.961
210	5.477	5.089	2.986	2.103
220	5.573	5.346	3.101	2.245
230	5.662	5.596	3.211	2.385
240	5.747	5.839	3.315	2.524
250	5.831	6.075	3.413	2.662
260	5.914	6.305	3.508	2.797
270	5.996	6.530	3.599	2.931
280	6.078	6.750	3.686	3.064
290	6.160	6.965	3.770	3.195
298.16	6.227	7.137	3.837	3.300
300	6.242	7.175	3.851	3.324

(10) K. K. Kelley, *U. S. Bureau of Mines Bulletin*, No. **476**, 121 (1949).

We thank Professor Leo Brewer and Dr. R. K. Edwards for treating the nickel sample *in vacuo* at high temperatures with subsequent careful annealing, Dr. T. H. Geballe for assistance with the heat capacity measurements and Drs. Paul D. Merica, E. M. Wise and G. L. Lee of the International Nickel Company for the specially prepared nickel sample used in this work.

BERKELEY, CALIFORNIA

[CONTRIBUTION NO. 184 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

The Heat Capacities and Heat Contents of Solutions of Cerium and Neodymium Chlorides at 25°

BY F. H. SPEDDING AND CARL F. MILLER

RECEIVED DECEMBER 26, 1951

The change in heat capacities of solution and dilution and the change in heat content of solution and dilution of the chlorides of cerium and neodymium have been measured for concentrations up to 0.35 and 0.40 molal, respectively. Both properties of these two electrolytes show agreement with the limiting Debye–Hückel equations within limits of experimental error.

Introduction

Previous studies on the solutions of rare earth compounds[2] have illustrated the need for further data on the physical properties of the rare earth elements and their compounds in regard to the role that they can play in checking physical chemistry theories.

The partial molal heat contents and partial molal heat capacities of higher charged electrolytes in solution should be sensitive to deviations from the ideal ionic solution and to deviations from the theoretical equations which describe these two properties due to such phenomena as association, changes in hydration of the ions, and compound formation. Since the charge on the ion is a constant factor for all the rare earth elements and the ionic radius of these elements is known to decrease with atomic number[3] the heat of solution of a given type of compound of these elements should increase with atomic number. Smaller ions of the same charge would, by presenting a relatively larger surface charge density to the surrounding water molecules, orient these water dipoles more strongly and to a greater degree than larger ions of like charge.

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2778 (1952).

(3) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).