THE ATOMIC HEAT CAPACITIES OF IRON AND NICKEL AT LOW TEMPERATURES

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In the collection of data on specific heats at low temperatures, it was noticed by one of the authors that the data on iron were extraordinarily discrepant. The results of Griffiths and Griffiths[1] and the results of Gunther[2] differ by as much as half a calorie at liquid-air temperatures, although the results of each can be fitted to the Debye curve. It seemed important to investigate the possibility that different samples of iron have widely different specific heats. The specific heat of nickel has also been determined, since the only data in the literature are determinations of mean specific heat over long ranges of temperature.

Experimental Part

The apparatus was similar to that used by Rodebush.[3] An adiabatic shield of polished copper was supported in the outer jacket by a short section of Pyrex tubing by means of three sets of small copper lugs placed edgewise. This shield was provided with a heating coil of No. 26 B. and S. Therlo wire and a copper-constantan thermocouple. The specimen of metal was hung in the center of the shield by a silk thread. The heating coil on the cylinder of the metal was of No. 36 B. and S. Therlo wire wound in a shallow thread turned on the metal. Thermal contact was insured by applying an alcoholic solution of shellac to the wire and drying after the excess had been removed. Two sets of leads were soldered to the heating coil, one set for the heating current and the other for potential measurements. A thermocouple of No. 36 Ideal wire and No. 35 copper wire was soldered to the sample of metal. The lead wires of No. 35 copper wire were protected from injury by a covering of silk threads knotted every few turns. This process was tedious but well worth while since the completed apparatus turned out to be remarkably rugged. It was possible to maintain an insulation resistance of several megohms between the various circuits. The lead wires were tied to the shield with silk thread and well paraffined to insure a good thermal contact.[4]

The electrical energy was measured by a Leeds and Northrup potentiometer and a stop watch. The current was kept at a known value during the

[1] Griffiths and Griffiths, *Proc. Roy. Soc.*, **88**, 549 (1913).

[2] Gunther, *Ann. Phys.*, **51**, 828 (1917).

[3] Rodebush, THIS JOURNAL, **45**, 1413 (1923).

[4] It was found by experiment that paraffin and shellac dried at room temperature do not become brittle enough at low temperatures to crack loose and destroy the thermal contact.

heating period by maintaining a constant IR drop across a known resistance. This drop was balanced against the e.m.f. of a Weston standard cell with several thousand ohms in series. The deflection of a sensitive galvanometer was kept at zero by a system of rheostats. Coarse adjustment was made by means of two ordinary slide-wire rheostats in parallel, and fine adjustment was made by means of a "Bradleystat" (0.25 to 100 ohms) in parallel with a 4-ohm fixed resistance. The current could be kept constant to better than 1 part in 10,000. An 8-volt lead storage-battery was used as a source of current.

Temperatures were read on a White potentiometer with a precision of 0.002°. Vacuum was maintained by a mercury-vapor pump. Pressures of the order of 0.00001 mm. were easily obtained in the low-temperature runs. At the temperatures obtained with solid carbon dioxide the pressure ran somewhat higher but remained low enough to avoid serious difficulties due to conduction.

The thermocouple wire was the same as that used by Rodebush[3] and was recalibrated in a somewhat different manner. The results were substantially in accord with the original calibration.

At low temperatures the oxygen vapor-pressure thermometer was used. Readings for the oxygen point were taken in a bath of liquid oxygen which was prepared by passing electrolytic oxygen through liquid air. A heating coil was used to keep the bath well stirred. Another point was taken in fresh liquid air. A third point was obtained by evaporating liquid air under reduced pressure, using a heating coil to keep the bath stirred. By means of the data of Henning and Heuse[5] on the vapor pressure of oxygen it was possible to determine the temperature to 0.1°.

Another point at the temperatures obtained with solid carbon dioxide was taken by means of the carbon dioxide vapor-pressure thermometer, using the data of Stock, Henning and Kuss.[6] This thermometer was similar to the oxygen thermometer. It was necessary to provide a reservoir of about 500 cc. to hold the evolved carbon dioxide when the apparatus was at room temperature. Carbon dioxide from a cylinder of the gas was passed through a solution of sodium carbonate and dried with phosphorus pentoxide. A considerable quantity was collected and the middle fraction of this was used to fill the thermometer. The bath for the determination consisted of a large test-tube of alcohol cooled by a slush of carbon dioxide snow and alcohol. It was necessary to stir the alcohol rapidly and to keep the slush well mixed in order to maintain a constant temperature.

The deviations from the table of Adams[7] were plotted against the readings in microvolts. The curve obtained was very smooth and did not

[5] Henning and Heuse, Z. Physik, **23**, 105 (1924).

[6] Stock, Henning and Kuss, Ber., **54**, 1119 (1921).

[7] Adams, "Pyrometry," Am. Inst. Mining Met. Eng., New York, **1920**, p. 170.

deviate greatly from a straight line. The values for dE/dT for any temperature were obtained by differentiating the equation of Adams and adding to this the slope of the deviation curve when the latter is plotted against temperature rather than against microvolts.

Specific-Heat Measurements

In making the measurements, the shield was heated to a predetermined point and then the block was heated for a four- or five-minute period while the current was kept constant and the voltage noted at intervals. The final temperature of the block then was.approximately the same as that of the shield, and a wait of ten minutes could be made without any loss of heat. Equilibrium was generally reached in about two minutes. The rise in microvolts was divided by the dE/dT for the average temperature and the rise in degrees obtained. The average rise was 2–2.5°. At the temperatures obtained with solid carbon dioxide it was necessary to apply a small correction ·for radiation from the shield being absorbed by the block. Thus, there is no chance for the block to lose heat because the surroundings are at least as hot as the block. Measurements at low temperatures show that there is no appreciable gain in heat. The gain in heat at the temperatures obtained with solid carbon dioxide is of the order of 0.5% of the total, so that a reasonable correction brings the error to a fraction of this. The specific heats of the organic matter, silver foil and heating coil were estimated from existing data to within a few per cent. Since the correction was from 1 to 2% of the total, an error of 10% in the estimate is not serious. The errors in energy input are negligible. Temperature measurements are accurate to 0.2%. The limit of precision is then about 0.5%.

The samples of iron and nickel were obtained from the Fatigue of Metals Laboratory of the Engineering Experiment Station through the courtesy of Professor Jasper. The iron was a well annealed sample of high grade, commercial iron which contained 99.88% of iron and small amounts of carbon, silicon, manganese and sulfur. The nickel was also annealed and consisted of 99+% of nickel with cobalt and iron as the chief impurities. These metals should have very little, if any, effect on the specific heat of the sample.

TABLE I

ATOMIC HEATS

IRON

Fe (151.85 g.) (Ag 1.375 g., Cu 0.33 g., Org. 0.145 g.)

Temp. °K.	C_s cal. per deg.	Temp. °K.	C_p cal. per deg.	Temp. °K.	C_p cal. per deg.
72.86	1.82	82.43	2.42	90.37	2.74
75.64	1.98	84.55	2.46	196.44	5.38
77.85	2.05	86.53	2.54	197.58	5.43
(80.00)	(2.19)	88.51	2.68	198.04	5.45
80.17	2.21	(90.00)	(2.73)	(200.00)	5.48

TABLE I (Concluded)

NICKEL

Ni (95.486 g.) (Ag 1.3715 g., Cu 0.416 g., Org. 0.252 g.)					
Temp. °K.	C_p cal. per deg.	Temp. °K.	C_p cal. per deg.	Temp. °K.	C_p cal. per deg.
67.85	1.871	80.20	2.480	95.19	3.120
(70.00)	(1.980)	82.33	2.585	97.41	3.200
70.55	2.028	85.19	2.690	99.64	3.275
73.16	2.133	87.85	2.805	(100.00)	(3.300)
75.66	2.262	(90.00)	(2.900)	101.80	3.357
78.01	2.368	90.39	2.925	103.94	3.428
(80.00)	(2.470)	92.78	3.007	106.00	3.470
195.93	5.47	199.46	5.47	203.20	5.53
196.22	5.53	199.70	5.54	....	...
197.71	5.50	(200.00)	(5.52)	....	...
198.15	5.50	201.45	5.54	....	...

Discussion

The results obtained for iron agree almost exactly with those of Griffiths and Griffiths. It should be noted that Gunther in his work used a special form of apparatus for iron which was not used for any other substance, so that his error is probably due to some defect in his apparatus. Lewis[8] has suggested that in the case of a hard metal such as iron the heat capacity might vary widely with the history of the specimen, but it seems doubtful whether this variation would be larger than the difference between C_p and C_v.

The results for nickel differ only slightly from those for iron, as might be expected.

The interpolation between the liquid-air measurements and absolute zero is readily made by superposing the experimental curve plotted on thin paper upon the Debye curve plotted to the same scale. The experimental values fell along the theoretical curve at low temperatures and so the experimental curve may be continued. The area under the curve then represents the entropy of the solid element. The value found for iron was 6.87 at 298° and that for nickel was 7.24 at 298°. These values are in good agreement with the calculations of Lewis, Gibson and Latimer.[8]

In Fig. 1 the values for C_v for the two metals are shown plotted against log T together with the theoretical curve of Debye (shown as the dotted line). The deviation from the Debye curve is marked at higher temperatures and is quite similar to the well-known deviations of the alkali metals.[9,10] This deviation has usually, in the case of the alkali metals, been ascribed to the presence of free electrons, but the question may very well be raised as to the possibility of its being due to crystal structure. Iron, in

[8] Lewis, Gibson and Latimer, THIS JOURNAL, 44, 1012 (1922).

[9] Eastman and Rodebush, ibid., 40, 481 (1918).

[10] Eastman, Williams and Young, ibid., 46, 1184 (1924).

common with the alkali metals, crystallizes in a body-centered lattice. The evidence in the case of nickel seems uncertain, but the resemblance of nickel to iron would lead one to assume a similar structure.   In the case
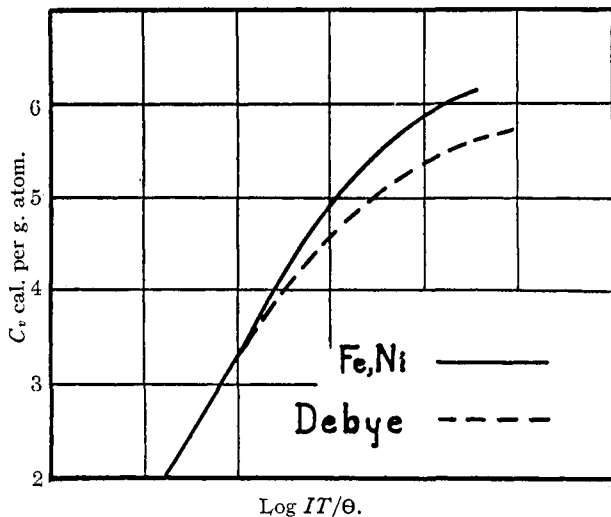
Log IT/Θ.
Fig. 1.

of the metals crystallizing in the hexagonal system, such as mercury,[11] a marked deviation from the Debye curve is found at low temperatures.

Summary

The atomic heat capacities of iron and nickel have been determined at low temperatures.   The work of Griffiths and Griffiths on iron is confirmed.

The relation between crystal structure of the metals and their deviations from the Debye curve is discussed.

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[11] Simon, Z. physik. Chem., 57, 279 (1923).