[Contribution from the Pacific Experiment Station, Bureau of Mines, United States Department of Commerce, in Coöperation with the University of California]

THE HEAT CAPACITY OF SILICON AT LOW TEMPERATURES[1]

By C. Travis Anderson[2]

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In continuation of its general program of determination of the heat capacities of the various metals and oxides which are important in metallurgical processes, the Pacific Experiment Station of the United States Bureau of Mines has studied an especially pure sample of metallic silicon.

The method and apparatus used in this work are identical with those described previously.[3]

The sample of silicon was furnished by the Electro Metallurgical Company of New York. According to their analysis, it had the following composition:

Si	99.20	C as Carbon	0.052
Fe	0.017	C as SiC	0.02
Al	0.009	Ni	Nil
Mn	Trace	Mg	Nil
Cu	Nil	O_2	0.17
Ca	<0.01	N_2	0.009
Ti	Nil		
Cr	Nil		99.48%

The analytic determination of silicon in this grade of material is difficult, and since the probable impurities are well accounted for, the sample may actually be 99.7% pure, *i. e.*, 100% minus the known impurities. A 139.8-g. sample was studied.

Screen tests were made, and the results are shown in Table I. The density of the silicon used was 2.34.

Table I

Screen Sizes of Silicon

Screen size	+65	+100	+150	+200	−200
Percentage	2.0	1.5	2.0	12.0	82.5

The Specific Heat

Measurements of the specific heat of silicon at low temperatures have previously been limited to six determinations of true specific heat by Nernst

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[3] Anderson, This Journal, **52**, 2296 (1930).

and Schwers[4] between 20 and 90°K., a few mean specific heats by Russell[5] from about 140 to 300°K., two determinations by Dewar[6] and a determination by Richards and Jackson.[7] The results of previous investigators are summarized and compared with the author's value in Table II.

Table II

The Gram Atomic Heat Capacity of Silicon

T, °K.	Mean T, °K.	C_p	Investigator	From author's curve
20.1		0.031	Nernst and Schwers	0.042
28.2		.086	Nernst and Schwers	.123
39.7		.248	Nernst and Schwers	.336
53.1		.548	Nernst and Schwers	.630
65.6		.826	Nernst and Schwers	.920
89.8		1.524	Nernst and Schwers	1.495
82.1 to 192.7	137.4	2.44	Russell	2.61
273.1 to 194.9	234.0	4.10	Russell	4.16
319.0 to 275.1	297.0	4.84	Russell	4.74
20 to 77 (melted)	48.5	0.86	Dewar	0.53
20 to 77 (cryst.)	48.5	0.77	Dewar	
85 to 293	189	3.34	Richards and Jackson	3.55

The results of Nernst and Schwers, the mean values of Russell and the mean value obtained by Dewar for the crystalline silicon are shown in Fig. 1. Richards and Jackson's result is not plotted as their temperature interval was unusually large. The results obtained in this Laboratory on the heat capacity of silicon expressed in gram calories (15°) per gram atom are given in Table III, and also are shown graphically in Fig. 1. In chang-

Table III

Heat Capacity per Gram Atom of Silicon

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
61.2	0.811	161.4	3.093	237.5	4.151
65.1	.974	164.3	3.116	241.4	4.236
75.0	1.160	165.8	3.187	246.6	4.299
88.4	1.453	179.5	3.406	253.3	4.431
98.8	1.695	186.9	3.539	258.2	4.383
116.7	2.162	192.5	3.575	265.9	4.893
129.8	2.443	196.0	3.678	283.3	4.680
133.6	2.519	199.2	3.735	287.0	4.703
145.5	2.760	205.3	3.807	290.4	4.685
157.1	2.983	213.6	3.901	294.5	4.671
158.8	3.020	222.8	4.011	296.3	4.652

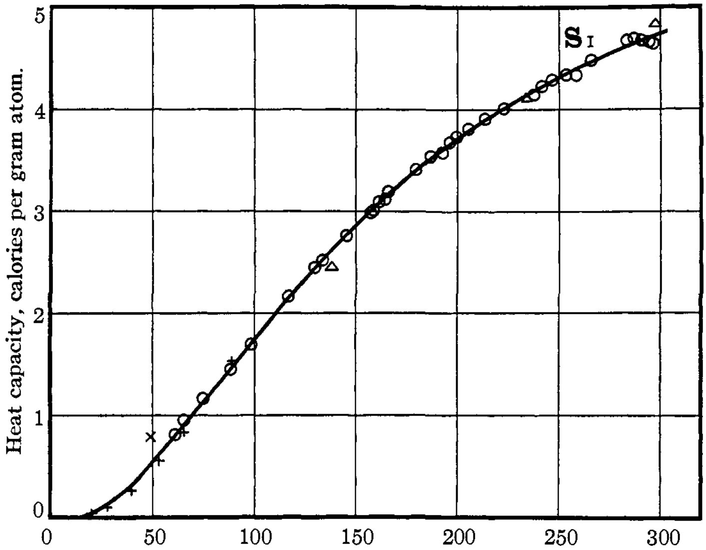
[4] Nernst and Schwers, "Berlin Akademie der Wissenschaften Sitzungsberichte," 355 (1914).

[5] Russell, *physik. Z.*, **13**, 59 (1912).

[6] Dewar, *Proc. Roy. Soc.* (London), **A89**, 158 (1913).

[7] Richards and Jackson, *Z. physik. Chem.*, **70**, 414 (1910).

ing joules to calories for the results of this table, the factor[8] 1/4.184 was used. The calculations were made on the basis of Si = 28.1. The accuracy of the data do not warrant correction for the impurities present, none of which are significant except the silicon dioxide, and the mass content and equivalent heat corrections nearly balance out in this case.



O, Anderson; +, Nernst and Schwers; △, Russell; ×, Dewar.

Fig. 1.—The heat capacity of silicon in calories per gram atom.

Calculation of Entropy.—The entropy was calculated in the conventional manner. The experimental heat capacity curve on a C_p-log T chart was extended below the lowest measurement and made to coincide with the Debye function having the parameter Θ = 441. The results of these entropy calculations are

Extrapolated (0–56.2) °K.	0.288
Graphical (56.2–298.1)	4.237
Total	4.52 ± 0.05 E. U.

The result, 4.5, differs by 0.2 E. U. from the value 4.7 given by Lewis and Randall[9] calculated from the meager data existing at that time, and is thought to be of better accuracy, especially in view of the high purity of the author's sample.

The author wishes to thank R. W. Millar for making three of the experimental determinations.

[8] "International Critical Tables," Vol. I, p. 24.

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 464.

Summary

The true heat capacity of silicon from 60 to 300°K. has been determined and its entropy at 298°K. calculated as 4.52 entropy units.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY AND THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, ALBANY MEDICAL COLLEGE]

THE FORMATION OF VITAMIN D BY MONOCHROMATIC LIGHT[1]

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It has now been demonstrated fairly conclusively by the work of Rosenheim and Webster[1a] and of Hess and Windaus[2] that ergosterol is the parent substance and apparently the only sterol from which it is possible to make a preparation by irradiation with light which is effective in curing rickets. Previous to this work it was thought that cholesterol was the provitamin, but this activity has been shown to be due to the presence of about 0.05% of ergosterol in the cholesterol, which can be destroyed by brominating the cholesterol.[1,2,3]

Several investigators have experimented with the effect of monochromatic light on cholesterol. Hess and Anderson,[4] using a quartz monochromator, concluded that the upper limit of wave length which gave any effect was 3130 Å. Light of wave length 2800 and 3020 Å. produced material of marked potency. The energy density of radiation was 3.9 ergs per second per sq. mm. but the total dose is not given. Sonne and Rekling[5] have rayed rats directly with lights of various frequencies obtained from a monochromator. The wave lengths used were 366, 313, 302–297, 280, 265, 254, 248 and 227–220$\mu\mu$ obtained from a mercury arc. The area rayed was 8.1 sq. cm. and the energy density varied from 5–0.3 $\times$ 10^{-4} g. calories per sq. cm. per minute. All the rats were rayed for thirty minutes daily. In the range 302–254$\mu\mu$ the rats were exposed to approximately 1.3 $\times$ 10^6 ergs daily and were protected from rickets by the light when fed McCollum's ricket producing diet; 248$\mu\mu$ and 240$\mu\mu$ were found to have less effect and 227$\mu\mu$ no effect. However, in the last three cases the energy used was considerably less than in those cases giving complete protection; 313$\mu\mu$ had only a doubtful action and

[1] A report of this work was presented at the Swampscott Meeting of the American Chemical Society, September, 1928.

[1a] Rosenheim and Webster, *Biochem. J.*, **21**, 389 (1927).

[2] Hess and Windaus, *Proc. Soc. Exptl. Biol. Med.*, **24**, 461 (1927).

[3] Windaus and Hess, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Klasse*, 175 (1926).

[4] Hess and Anderson, *J. Am. Med. Assocn.*, **89**, 1222 (1927).

[5] Sonne and Rekling, *Strahlentherapie*, **25**, 552 (1927).