Feytis.[4] However, she did not find this effect at elongations below 400%, which is greater than any employed here. Since she only reports the period of oscillation in and out of the field for the Krishnan oscillation method, and does not report the actual anisotropies of her rubber samples, it is impossible to tell whether or not her results at lower elongations agree with those found here.

Finally, the change in anisotropy with time, at any one elongation, was found to be small at all elongations, at least for Natural Rubber, and the changes were almost the same for each elongation and therefore would not change the slope of the curve showing the change of anisotropy with elongation.

Evanston, Illinois Received October 20, 1951

[Contribution from the Chemical Laboratory of the University of California]

The Heat Capacity and Entropy of Gold from 15 to 300°K.[1]

By T. H. Geballe and W. F. Giauque

Received January 8, 1952

The heat capacity of single crystal gold has been measured from 15 to 300°K. The heat capacity at constant volume has been calculated and compared with the Debye equation, which is used only as an idealized reference curve. The results, compared with those on several other face centered cubic metal crystals, show that the distribution of vibrational frequencies is characteristic of each metal. This is in agreement with the theoretical expectations of Blackman. The entropy, heat content and free energy have been tabulated. The entropy, less nuclear spin and isotope effects, was found to be 11.32 ± 0.02 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

Some years ago the heat capacities of single crystals of aluminum, copper,[2] silver and lead[3] were measured from 15–300°K. These metals were selected for comparison because they were all face centered cubic structures.

A crystal of gold was prepared at about the same time but heat capacity measurements, which were postponed by the war, were completed only recently. The calorimeter and the procedure for preparing the crystal were the same as those used previously.[2] The temperature scale was in terms of a standard copper–constantan thermocouple, with the laboratory designation W-26, which was originally calibrated against a helium gas thermometer. It was checked against the triple point (13.92°K.) and boiling point (20.36°K.) of hydrogen, and the triple point of nitrogen (63.15°K.) just before the present experiments. The comparison was made in a manner that permitted the simultaneous calibration of the resistance thermometer and thermocouple at the above points.

The gold was obtained from the American Platinum Works, Newark, New Jersey, and was stated to be 99.99% pure. Analyses made by Dr. W. R. Forsythe in this Laboratory showed that silver, copper and iron if present were less than 0.001% each. The crystal investigated had a weight of 2504.12 g. *in vacuo*. The melted gold was solidified over a period of about 12 hours in the apparatus described previously[2] for the preparation of single crystals. The molecular weight was taken as 197.2.

The observed data are given in Table I. One calorie is taken as 4.1840 absolute joules. The runs were made in two series and the observations were continuous in the sense that each run started where the previous one ended. Thus the range was completely investigated. A smooth curve through the data is believed to be accurate to 0.1 to 0.2% above 35°K., at 20°K. the error may be 1%, and at 15° it may be 3% due to decreasing sensitivity of the resistance thermometer.

Table I

Heat Capacity of Gold, Cal. Deg.$^{-1}$ (G. Atom)$^{-1}$

Atomic Wt. = 197.2; 0°C. = 273.16°K.

T, °K. Average	C_p	*T*, °K.	C_p	*T*, °K.	C_p
Series I		108.65	5.257	253.81	5.970
15.81	0.402	116.89	5.341	263.63	5.992
18.35	.629	125.05	5.411	272.47	6.005
21.16	.873	133.54	5.489	Series II	
24.70	1.210	142.25	5.555	205.46	5.864
29.19	1.672	150.88	5.624	211.14	5.876
34.76	2.226	159.58	5.673	220.50	5.888
40.12	2.687	167.82	5.711	230.01	5.906
45.17	3.072	176.12	5.755	239.82	5.928
50.98	3.470	184.40	5.785	249.95	5.957
57.41	3.848	192.70	5.805	259.68	5.980
63.85	4.145	202.79	5.848	269.96	6.005
70.66	4.406	211.30	5.849	280.20	6.022
78.27	4.650	219.92	5.880	288.41	6.044
85.67	4.835	228.60	5.900	298.46	6.089
93.19	4.984	237.38	5.916	309.02	6.095
100.82	5.132	246.12	5.948		

The heat capacity of gold has been measured by Clusius and Harteck[4] from 15 to 211°K. They do not give the purity or physical state of their gold sample. Over the ranges 15 to 35°K. and 70 to 90°K. their results agree quite well with the present measurements. Between 35 and 70° their results are several per cent. high and from 90 to 211°K. about 1% high. However, the particular calorimeter which they used was not well adapted for observations at temperatures considerably different from that of the bath, an effect which is not uncommon in earlier work. Their results near the temperatures of liquid hydrogen and liquid air are the ones in good agreement.

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(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) P. F. Meads, W. R. Forsythe and W. F. Giauque, *ibid.*, **63**, 1902 (1941).

(4) K. Clusius and P. Harteck, *Z. physik. Chem.*, **134**, 243 (1928).

C_V is more directly comparable to theoretical expressions than C_P, thus the values of C_V have been computed with the assistance of the equation

$$C_P - C_V = \alpha^2 VT/\beta$$

where α and β represent the coefficients of cubical expansion and compressibility, respectively, and V is the volume per g. atom.

The value of α for 25° was taken as 42.8×10^{-6} deg.$^{-1}$ from the I.C.T.[5] and the compressibility from Bridgman.[6]

$$\beta = 5.60 \times 10^{-7} \text{ atm.}^{-1} \text{ at } 25°$$

Since values of α and β at various temperatures are incompletely known, the corrections below room temperature were made by means of the empirical equation $C_P - C_V = ATC_P^2$ where A is a constant.

Values of C_V computed by means of α^2VT/β apply to the particular volume existing at each temperature. It would be desirable to compute values of C_V which applied to one particular volume through use of the thermodynamic equation

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial(\alpha/\beta)}{\partial T}\right)_V$$

Giauque and Meads[2] investigated this question in other cases and found that the correction was negligible. It may be shown that for gold the effect is less than 0.1% even for the volume change between the absolute zero and 300°K.

The results are compared with the Debye heat capacity equation in Table II. This is done only because the Debye equation represents an idealized, quantized, structureless solid which makes a useful reference.

In order to show the way in which structural details affect heat capacity, the Debye curve should be brought into coincidence with the actual data at a very low temperature where relatively long waves and blurred structural effects correspond to its conditions. This is impracticable in the present case because the data extend only to 15°K. If it could be done the agreement in the sensitive range where the curve is rising rapidly would be poor. As the high temperature limiting value of $3R$ is approached the curve is again insensitive to structure. In Table II the data are brought into coincidence with the Debye curve at a point where $C_V = 3R/2$, thus this sensitive portion of the curve is forced into rather good agreement. Table II also includes values of entropy, heat content and free energy.

The heat capacity of gold resembles that of silver rather than lead with respect to the temperature at which it decreases rapidly. C_V for Ag = $3R/2$ at 52.9°K., whereas, C_V for Au = $3R/2$ at 44.05°K.

TABLE II

THERMODYNAMIC PROPERTIES OF GOLD, CAL. DEG.$^{-1}$ G. ATOM^{-1}

0°C. = 273.16°K. Atomic wt. 197.2

T, °K.	C_P	C_V	C_V/C_{Deb}	S	$\frac{H^0 - H^0_0}{T}$	$-\frac{F^0 - H^0_0}{T}$
15	0.354	0.354	1.264	0.120	0.091	0.029
20	.768	.768	1.215	.278	.208	.070
25	1.242	1.242	1.122	.499	.366	.133
30	1.758	1.756	1.073	.771	.555	.216
35	2.247	2.243	1.040	1.078	.762	.316
40	2.678	2.672	1.014	1.407	.975	.432
45	3.063	3.054	0.999	1.745	1.186	.559
50	3.409	3.396	.992	2.084	1.392	.692
60	3.973	3.952	.988	2.760	1.776	.984
70	4.388	4.358	.987	3.405	2.123	1.282
80	4.692	4.653	.986	4.011	2.425	1.586
90	4.927	4.887	.987	4.576	2.690	1.886
100	5.116	5.064	.988	5.109	2.925	2.184
110	5.264	5.197	.989	5.603	3.131	2.472
120	5.372	5.296	.988	6.065	3.313	2.752
130	5.458	5.373	.987	6.500	3.475	3.025
140	5.541	5.446	.988	6.907	3.619	3.288
150	5.615	5.511	.990	7.295	3.751	3.544
160	5.676	5.563	.991	7.656	3.868	3.788
170	5.727	5.604	.992	8.003	3.977	4.026
180	5.770	5.638	.992	8.331	4.075	4.256
190	5.807	5.667	.992	8.643	4.165	4.478
200	5.840	5.690	.992	8.941	4.247	4.694
210	5.867	5.708	.992	9.228	4.325	4.903
220	5.887	5.719	.991	9.501	4.395	5.106
230	5.908	5.731	.990	9.763	4.461	5.302
240	5.933	5.747	.990	10.015	4.520	5.495
250	5.957	5.762	.991	10.257	4.579	5.678
260	5.981	5.776	.991	10.492	4.632	5.860
270	6.005	5.791	.992	10.718	4.682	6.036
280	6.028	5.804	.993	10.937	4.730	6.207
290	6.049	5.815	.994	11.149	4.775	6.374
298.16	6.066	5.825	.994	11.318	4.810	6.508
300	6.070	5.827	.994	11.355	4.818	6.537

While the combined effects of mass and interatomic forces bring the dominating frequencies of gold and silver into the same range, it is evident from a comparison of C_V/C_{Debye} with the similar tabulation of Meads, Forsythe and Giauque,[3] that the vibrational frequency spectrum of these two metals is quite different. A comparison of the data on aluminum, copper, silver, lead and gold makes it clear that there is no possibility of representing the heat capacities of these face centered cubic crystals by an equation with a single parameter.

This is in agreement with the theoretical conclusions of Blackman[7] who points out that while the very low temperature heat capacity depends on the elastic constants, the values at high temperatures are controlled by a vibrational spectrum which is characteristic of the substance and is not related in any simple way to values derived from the elastic constants.

We thank Dr. R. H. Busey for assistance with the experimental measurements and Dr. W. R. Forsythe for analyzing the gold.

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