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

The Heat Capacities and Entropies of Aluminum and Copper from 15 to 300°K.

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The heat capacities of gases can often be calculated from molecular data more accurately than they can be obtained by direct measurement but this has not yet been found possible for even the simplest crystalline solids. The equation which has been of greatest use for atomic solids is that of Debye[1]; however, this equation takes no account of structure in solids except in that an upper limit of the fundamental frequencies is introduced corresponding to the vibration of a single atom.

It has long been evident that a solution of this problem must start with a knowledge of the structural details and work toward the region of lower frequencies where structure is of little importance rather than the reverse procedure. The necessity for this approach is especially evident when one considers that approximately 85% of the degrees of freedom are concerned with modes of motion which may, to a good approximation, be thought of as involving motions of three or less atoms. In other words, the principal features of a heat capacity curve during the rapidly rising portion are concerned largely with modes of motion in which the specific nature of the atomic arrangement and binding are important.

Attacks on this problem on the above lines have been made by Born and Karman,[2] Blackman,[3] and more recently by Fine.[4]

The only case in which the heat capacity has been calculated from elastic constants with reasonable accuracy is that of tungsten. This element which crystallizes in a body-centered cubic lattice has been considered by Fine who obtains fair agreement with the available observations. Fine made certain assumptions such as harmonic oscillations and elastic constants independent of temperature which would appear to account for such deviations as remain between theory and experiment.

In undertaking the present measurements, which were made before the recent theoretical advances of Blackman and Fine, it appeared desirable to investigate several metals each in the same crystal system to see the extent to which one type of atomic arrangement might be represented by a characteristic heat capacity curve. The data are also desirable in that they enable the calculation of accurate values of the entropies of the several substances.

Four metals, each with a face centered cubic crystal lattice, were selected for investigation: aluminum, copper, silver and lead. The data on the first two substances will be given here and the latter two in a following paper,[5] which will include the comparison of all the data. It is not unusual for authors to neglect, or at any rate fail to mention, the physical state of the material investigated despite the fact that differences in thermodynamic properties often exist. It seemed desirable to use well known single crystal technique in preparing thermodynamically stable samples. This was done.

The aluminum was supplied to us through the courtesy of the Research Laboratory of the Aluminum Company of America. Their analysis gave the purity as 99.944% and it was stated that the metal could be melted in a crucible of Acheson graphite without contamination.

A crucible in the form of a cylinder of the size sample desired for the calorimeter was made with an upper compartment for melting the metal. The lower compartment was made with a small bore hole extending below the conical bottom. The crucible was surrounded by several independently controlled wire wound heating elements and the whole enclosed in a large iron bell jar which could be evacuated. On melting, the metal ran through a small hole into the lower part of the crucible. The current through the heaters was then controlled so that solidification started at the bottom and advanced up the small tube into the main body of the sample. Thermocouples were arranged in holes drilled into the side of the crucible at intervals. Solidification and cooling took place over a period of two days. When the cylinder was removed it became evident that a small amount of aluminum carbide had been formed on the surface. This was removed by dissolving away the exterior of the sample. Examination under a microscope, after polishing and etching a longitudinal strip, did not show any phase boundaries in the crystal. The aluminum sample weighed 266.37 g. = 9.877 g.-atoms.

The copper was a Bureau of Standards standard temperature sample (Lot 45a) and the purity was stated to be better than 99.96%. The sample was prepared in the

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(1) Debye, *Ann. Physik*, **39**, 789 (1912); **43**, 49 (1914).

(2) Born and Karman, *Physik. Z.*, **13**, 297 (1912); **14**, 15 (1913).

(3) Blackman, *Proc. Roy. Soc.* (London), **A148**, 365, 384 (1935); **A149**, 117, 126 (1935).

(4) Fine, *Phys. Rev.*, **56**, 355 (1939).

(5) Meads, Forsythe and Giauque, THIS JOURNAL, **63**, 1902 (1941).

apparatus and manner used for aluminum except that an atmosphere of nitrogen was used instead of a vacuum around the furnace. The solidification and annealing was carried out over a period of five days. The sample weighed 825.24 g. = 12.982 g.-atoms.

The calorimetric apparatus was very similar to that described by Giauque and Egan[6] except that it contained a built-in hydrogen liquefier[7] and did not include the several features relating specifically to the investigation of condensed gases.

The calorimeter was made of copper. It was 11 cm. long and 4.5 cm. in diameter. The wall thickness was 0.045 cm. The top was made so that it could be entirely removed. After the block of metal had been placed in the calorimeter the cover was soldered into place with a low melting solder. A small hole in the cover allowed helium to be introduced at one atmosphere at room temperature to assist in attaining thermal equilibrium.

TABLE I

HEAT CAPACITY OF ALUMINUM

Atomic weight, 26.97; 0°C. = 273.10°K.

T, °K., average	C_p cal. deg.$^{-1}$ g.-atom^{-1}	T, °K., average	C_p, cal. deg.$^{-1}$ g.-atom^{-1}
15.29	0.024	148.50	4.391
17.68	.037	153.54	4.492
20.08	.055	158.60	4.579
22.67	.081	163.66	4.683
27.01	.145	167.26	4.754
31.61	.243	172.78	4.809
35.94	.360	178.45	4.899
40.68	.522	183.79	4.968
45.98	.736	189.05	5.033
51.11	.968	194.06	5.099
55.18	1.157	199.45	5.161
58.59	1.316	204.92	5.212
61.90	1.472	209.38	5.243
65.79	1.654	210.52	5.285
70.16	1.861	214.35	5.283
70.52	1.878	216.53	5.326
74.66	2.075	220.40	5.335
79.35	2.280	225.75	5.376
84.00	2.484	231.37	5.421
88.52	2.672	236.95	5.480
93.63	2.884	242.44	5.514
97.97	3.062	247.80	5.534
102.24	3.193	253.32	5.572
106.65	3.331	257.99	5.604
111.17	3.475	263.44	5.641
115.78	3.621	268.80	5.653
119.44	3.744	273.03	5.691
119.74	3.748	278.57	5.724
124.85	3.868	284.01	5.743
129.77	3.995	289.65	5.806
134.95	4.112	295.40	5.813
138.91	4.202	295.94	5.801
143.55	4.302	301.60	5.853

The outer wall of the calorimeter was wound from the bottom to within 2 cm. of the top with a gold resistance thermometer of the type previously described.[6] A standard thermocouple,[8] with the laboratory designation no. 103, was soldered to the bottom of the calorimeter. During the course of the measurements the thermocouple was checked against the triple and boiling points of hydrogen and agreement was found within a few hundredths of a degree. This comparison was made with the thermocouple in place in the calorimetric apparatus by filling the space surrounding the calorimeter with liquid hydrogen.

The experimental data are given in Tables I and II. The end temperature of one measurement was the starting temperature of the one following so there were no uninvestigated intervals. One calorie was taken as 4.1833 international joules.

TABLE II

HEAT CAPACITY OF COPPER

Atomic weight 63.57, 0°C. = 273.10°K.

T, °K., average	C_p, cal. deg.$^{-1}$ g.-atom^{-1}	T, °K., average	C_p, cal. deg.$^{-1}$ g.-atom^{-1}
14.70	0.040	151.01	4.924
14.82	.040	156.91	5.000
17.63	.072	162.77	5.066
19.75	.107	168.28	5.157
19.87	.110	174.05	5.187
23.35	.187	179.36	5.240
28.21	.340	184.72	5.302
33.52	.570	190.18	5.343
38.86	.840	195.81	5.396
44.21	1.137	201.39	5.434
48.17	1.382	207.07	5.483
53.34	1.697	213.03	5.534
59.08	2.023	218.90	5.540
65.12	2.345	224.23	5.579
70.12	2.605	229.66	5.603
75.36	2.876	235.25	5.636
80.60	3.118	240.71	5.673
85.62	3.326	245.98	5.704
90.73	3.513	251.58	5.728
95.78	3.704	256.60	5.734
101.24	3.893	261.34	5.757
106.72	4.059	266.61	5.779
112.25	4.210	272.18	5.790
117.86	4.327	277.69	5.820
123.40	4.458	283.59	5.831
128.99	4.554	289.51	5.827
134.54	4.655	294.76	5.854
140.20	4.753	300.15	5.840
146.02	4.843		

Heat capacity values taken at even temperatures from smooth curves through the data are given in Tables III and IV. Values of C_v, the atomic heat capacity at constant volume, are also

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(6) Giauque and Egan, *J. Chem. Phys.*, **5**, 1 (1937).

(7) Liquefiers built into calorimetric equipment are no longer used in this laboratory in order to reduce the extent of the high pressure hydrogen system for reasons of safety and because the transfer of liquid hydrogen to apparatus is a simpler procedure.

(8) (a) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

given. The difference, $C_p - C_v$, was calculated at room temperature from the thermodynamic formula

$$C_p - C_v = \alpha^2 VT/\beta \qquad (1)$$

where α is the coefficient of cubical thermal expansion, V the molal volume and β the coefficient of cubical compressibility. At other temperatures $C_p - C_v$ was obtained with the assistance of the empirical relation

$$C_p - C_v = AT\,C_p^2 \qquad (2)$$

The values of A used were

Aluminum, $A = 2.23 \times 10^{-5}$ g.-atom cal.$^{-1}$
Copper, $A = 1.78 \times 10^{-5}$ g.-atom cal.$^{-1}$

Equation 1 gives C_v for the particular volume corresponding to each temperature. The change of C_v with volume can be calculated from the thermodynamic equation

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = T\left(\frac{\partial\left(\frac{\alpha}{\beta}\right)}{\partial T}\right)_V$$

$$\Delta C_v = \int T\left(\frac{\partial\left(\frac{\alpha}{\beta}\right)}{\partial T}\right)_V \mathrm{d}V \qquad (3)$$

The change of C_v with volume was found to be negligible. In column 4 of Tables III and IV the values of C_v are compared with those calculated from the Debye equation by computing the ratio C_v(obsd.)/C_v(calcd.). The comparison is made in this way, not to test the Debye function which is well known to be only a first approximation but because this function represents a certain idealized limit and thus makes a very useful curve of reference. The ratios will be used to compare the results on aluminum, copper, silver and lead in the following paper.[5] In columns 5, 6 and 7 of Tables III and IV the entropy, S, the heat content given as $(H - H^0_0)/T$ and the free energy as $(F - H^0_0)/T$ are presented. The values

TABLE III

THERMODYNAMIC PROPERTIES OF ALUMINUM

Cal. deg.$^{-1}$ g.-atom^{-1} 0°C. = 273.10°K. Atomic wt. 26.97

T, °K.	C_p	C_v	C_v/C_v Debye	S	$(H - H^0_0)/T$	$-(F - H^0_0)/T$
15	0.022	0.022	0.827	0.007	0.005	0.002
20	.054	.054	.856	.017	.013	.004
25	.112	.112	.910	.035	.026	.009
30	.203	.203	.957	.063	.048	.015
35	.332	.332	.995	.103	.079	.024
40	.500	.500	1.024	.158	.121	.037
45	.698	.698	1.037	.229	.173	.056
50	.913	.912	1.033	.313	.236	.077
60	1.378	1.375	1.020	.520	.388	.132
70	1.851	1.846	1.008	.768	.563	.205
80	2.307	2.298	1.002	1.046	.753	.293
90	2.729	2.714	0.998	1.342	.949	.393
100	3.116	3.094	1.000	1.650	1.147	.503
110	3.451	3.422	0.999	1.964	1.342	.622
120	3.741	3.704	0.998	2.279	1.530	.749
130	3.989	3.943	1.000	2.586	1.710	.876
140	4.221	4.165	0.999	2.891	1.881	1.010
150	4.427	4.361	1.001	3.189	2.044	1.145
160	4.612	4.536	1.006	3.481	2.198	1.383
170	4.776	4.690	1.009	3.765	2.344	1.421
180	4.920	4.823	1.011	4.043	2.484	1.559
190	5.045	4.938	1.013	4.311	2.616	1.695
200	5.158	5.039	1.015	4.572	2.740	1.832
210	5.251	5.122	1.015	4.826	2.858	1.968
220	5.338	5.198	1.015	5.073	2.968	2.105
230	5.418	5.268	1.016	5.312	3.073	2.239
240	5.490	5.329	1.016	5.544	3.173	2.371
250	5.557	5.383	1.017	5.769	3.267	2.502
260	5.619	5.436	1.018	5.989	3.356	2.633
270	5.677	5.483	1.019	6.202	3.447	2.755
280	5.728	5.523	1.019	6.409	3.522	2.887
290	5.778	5.562	1.020	6.610	3.599	3.011
298.1	5.817	5.592	1.020	6.769	3.668	3.101
300	5.826	5.599	1.021	6.806	3.672	3.134

TABLE IV

THERMODYNAMIC PROPERTIES OF COPPER

Cal. deg.$^{-1}$ g.-atom, 0°C. = 273.10°K., Atomic wt. 63.57

T, °K.	C_p	C_v	C_v/C_v Debye	S	$(H - H^0_0)/T$	$-(F - H^0_0)/T$
15	0.041	0.041	0.801	0.013	0.010	0.003
20	.114	.114	.939	.034	.026	.008
25	.233	.233	.987	.072	.055	.017
30	.412	.412	1.026	.129	.099	.030
35	.637	.637	1.033	.209	.159	.050
40	.901	.901	1.033	.311	.236	.075
45	1.191	1.190	1.029	.434	.325	.109
50	1.493	1.491	1.025	.575	.427	.148
60	2.074	2.069	1.009	.899	.654	.245
70	2.615	2.606	1.002	1.260	.896	.364
80	3.091	3.077	0.999	1.641	1.141	.500
90	3.500	3.480	.999	2.034	1.381	.653
100	3.847	3.821	.999	2.421	1.611	.810
110	4.138	4.104	1.000	2.798	1.828	.970
120	4.380	4.339	1.000	3.168	2.031	1.137
130	4.580	4.531	0.999	3.527	2.219	1.308
140	4.752	4.696	0.999	3.874	2.394	1.480
150	4.904	4.840	1.000	4.207	2.557	1.650
160	5.042	4.970	1.002	4.527	2.708	1.819
170	5.163	5.082	1.004	4.836	2.849	1.987
180	5.263	5.174	1.005	5.134	2.980	2.154
190	5.350	5.253	1.005	5.421	3.103	2.318
200	5.430	5.325	1.006	5.699	3.217	2.482
210	5.499	5.386	1.007	5.965	3.324	2.641
220	5.558	5.437	1.007	6.222	3.424	2.798
230	5.613	5.484	1.007	6.470	3.519	2.951
240	5.670	5.532	1.009	6.710	3.607	3.103
250	5.719	5.573	1.010	6.943	3.690	3.253
260	5.755	5.601	1.009	7.168	3.769	3.399
270	5.788	5.627	1.009	7.386	3.843	3.543
280	5.817	5.648	1.008	7.597	3.913	3.684
290	5.837	5.661	1.006	7.801	3.979	3.822
298.1	5.848	5.666	1.004	7.961	4.030	3.931
300	5.850	5.667	1.003	7.999	4.042	3.957

at 15°K. were obtained by extrapolation to 0°K. The amounts concerned are so small that there is little uncertainty due to this procedure. The values of entropy and free energy are, as usual, given without inclusion of the nuclear spin and isotope contributions which cancel in chemical reactions.

Comparisons with the Debye curve have been made by many authors by calculating a value of the characteristic temperature, θ, of the function for each observation and we also tried this method of representing the data. However, the accuracy with which θ can be obtained from observations of equal accuracy varies widely with the temperature and it was decided that the ratios are much to be preferred in representing the deviations. Moreover, when the heat capacity exceeds the limiting value of the Debye function it is obviously impossible to calculate a θ.

In selecting the θ to be used for the reference function, the temperature at the point where the experimental C_v curve passed through the value $C_v = {}^3/_2R = 2.980$ cal. deg.$^{-1}$ g.-atom^{-1} was assumed to lie on a Debye curve. For aluminum this temperature was 96.8°K. leading to a $\theta = 389.1$. For copper the values were $T = 77.8$°K., $\theta = 312.8$.

The smooth curves through the data are believed to be accurate to 0.1 to 0.2% above 35°K., at 20° the error may be 1% and at 15° the error may be 2 or 3% due to decreasing sensitivity of the resistance thermometer.

The earlier data on the heat capacity of aluminum have been summarized by Rodebush and Rodebush,[9] who estimated the accuracy at about 5%, however, the smoothed values which they selected are in fortuitous agreement with the present results to within a few tenths of a per cent. except at 50°K. where their selected value is 2% low. Kok and Keesom[10] measured the heat capacity of aluminum from 1.1 to 20°K. They used a block of metal 99.7% pure and did not specify its physical history. The curve through their data lies about 7% below the present measurements at 10° and 20% below at 15°. These differences are probably to be explained by the effect of impurity and physical state rather than by experimental error.

The heat capacity of aluminum has also been measured at the U. S. Bureau of Mines Station at this University by Maier and Anderson[11] who compared their results with the present data.[12] Maier and Anderson measured hard drawn and annealed aluminum wire from 55 to 295°K. and we quote from their comparison that the annealed aluminum averaged 0.025 cal. deg.$^{-1}$ g.-atom^{-1} below, and the hard drawn aluminum 0.034 cal. deg.$^{-1}$ g.-atom^{-1} below our results for single crystal aluminum. Before commenting on these results it will be desirable to consider similar results on copper.

The heat capacity of copper has been measured by Griffiths and Griffiths[13] and by Keesom and Kamerlingh Onnes.[14] These early results are not quite as accurate as the more recent work. Eucken and Werth,[15] Maier and Anderson[11] and Dockerty[16] have all made accurate heat capacity measurements on variously treated samples of copper.

Eucken and Werth made measurements on recrystallized and on beaten copper; they found no difference within their limits of accuracy. Their measurements, which extend from 84 to 215°K., agree with our results on single crystal copper to within a few tenths of a per cent. except between 80 and 100°K. where they are 1 to 2% low.

Dockerty measured "commercially pure cold rolled copper" and Maier and Anderson used fine wire (0.0075 inch in diam.) hard drawn and also annealed. All of these results and the present data agree within less than 0.5%.

Maier and Anderson[11] consider that their results indicate no difference in heat capacity for hard drawn annealed or single crystal copper and suggest that the differences have their origin in the different methods of applying corrections due to heat received from or given to the calorimeter surroundings. They emphasize the agreement at the temperature of liquid air where corrections are small. However, the calorimeters used by Maier and Anderson and in the present research are very similar and we believe that one can attach some significance to the difference in the results. Admitting that uncertainty increases somewhat with the increasing magnitude

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[9] Rodebush and Rodebush, "I. C. T.," Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1929, p. 87.

[10] Kok and Keesom, *Comm. Phys. Lab. Leiden*, No. 248e (1937).

[11] Maier and Anderson, *J. Chem. Phys.*, **2**, 513 (1934).

[12] The measurements reported here were made in 1931.

[13] Griffiths and Griffiths, *Trans. Roy. Soc.* (London), **A214**, 319 (1914).

[14] Keesom and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 143 (1914), No. 147a (1915).

[15] Eucken and Werth, *Z. anorg. Chem.*, **188**, 152 (1930).

[16] Dockerty, *Can. J. Research*, **15**, 59 (1937).

of the heat transfer corrections one would expect that errors at the higher temperatures would lead to divergences which are somewhat proportional to T^3. However, the differences at 300°K. are not about eight times those at 150°K. but remain more nearly constant.

The tendency is for the more perfect crystalline samples to have the higher heat capacity. This does not seem unreasonable in view of the fact that working copper makes it hard.

For aluminum Maier and Anderson estimate that the heat capacity of the single crystal sample averages about 0.8% higher than hard drawn wire over the interval 50–300°K. We consider this to be outside the limit of error of the calorimeters used by Maier and Anderson, and in the present work. Maier and Anderson used the temperature scale obtained with the gas thermometer in this Laboratory but it is important to realize that temperature scale differences are not important when regions of 200 or 300° are used in averaging. It is improbable that any one temperature on any of the scales used by the several experimenters would be off sufficiently to cause more than a difference of some hundredths of a per cent. over the whole interval although results in various regions might well vary by considerably more than this amount due to temperature scale differences.

Maier and Anderson, and Dockerty, measured the density of their copper samples and Dr. Maier[17] has since kindly measured the density of the single crystal copper sample used in this research. The heat capacity and density results are summarized in Table V. Dockerty's results extend only to 194°K. but the deviation is extraordinarily consistent and we have assumed that it would continue to ordinary temperatures in arriving at the comparison made in Table V. For the other heat capacity comparisons we have accepted the estimate of Maier and Anderson.

TABLE V

EFFECT OF CRYSTAL PERFECTION ON THE PROPERTIES OF COPPER

ΔC_p in cal. deg.$^{-1}$ g.-atom^{-1} averaged from 50–300°K., $\Delta C_p = C_p - C_p$ single crystal

Sample	ΔC_p	Den., g./cc.	Observer
Single crystal	(0.000)	8.9528	Giauque and Meads
Annealed wire	−0.009	8.9209	Maier and Anderson
Cold rolled bar	− .018	8.91	Dockerty
Hard drawn wire	− .20	8.9140	Maier and Anderson

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Summary

The heat capacities of single crystal aluminum and copper have been measured from 15 to 300°K.

The results have been compared with existing data on samples subjected to cold working.

The heat capacity of the single crystal samples is slightly higher than that of the harder forms produced by cold working.

The entropy of aluminum was found to be 6.77 cal. deg.$^{-1}$ g.-atom^{-1} at 25°C. The entropy of copper is 7.97 cal. deg.$^{-1}$ g.-atom^{-1} at 25°C. These entropy values do not include the entropy due to nuclear spin and isotopic mixing and thus are the values to be used in ordinary thermodynamic calculations.

Tables of free energy and heat content are given for aluminum and copper to 300°K.

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[17] Personal communication from Dr. C. G. Maier.