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

The Heat Capacities and Entropies of Silver and Lead from 15° to 300°K.

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The work presented here is a continuation of the heat capacity measurements reported in the previous paper[1] together with a discussion of all the results.

The same single crystal technique described for preparing samples of aluminum[1] and copper[1] was used to prepare similar samples of silver and lead. Electrolytic silver 99.99% pure was melted and crystallized in an atmosphere of nitrogen and cooled over a period of five days. The sample weighed 1066.69 g. = 9.888 g.-atoms.

Lead containing no silver or bismuth and but 0.001% of iron was used. Lead oxide was removed by a preliminary melting with fused sodium hydroxide. The oxide free lead was then melted and crystallized in the form of a suitable cylinder in a vacuum furnace. The cooling extended over a period of four days. The weight of the lead was 1162.84 g. = 5.6116 g.-atoms.

Table I

Heat Capacity of Silver

Atomic weight 107.880; 0°C. = 273.10°K.

T, °K.	C_p, cal. deg.$^{-1}$ g.-atom^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ g.-atom^{-1}
Crystal made 5-12-31 to 5-16-31			
Series 1, Calorimeter 1, 6-12-31			
63.78	3.603	180.96	5.716
67.94	3.807	186.45	5.743
73.02	4.030	192.04	5.776
78.13	4.231	197.96	5.797
83.28	4.389	203.43	5.820
88.50	4.533	209.10	5.849
93.63	4.665	215.06	5.882
98.88	4.803	220.86	5.875
104.06	4.915	226.50	5.895
109.09	5.017	232.30	5.919
114.24	5.088	238.25	5.945
119.53	5.174	244.03	5.975
124.95	5.209	249.65	5.989
130.53	5.280	255.40	6.005
136.27	5.352	260.36	6.026
141.77	5.409	265.83	6.033
145.44	5.445	271.20	6.058
149.50	5.506	276.83	6.079
154.40	5.524	282.51	6.095
159.45	5.564	288.11	6.111
164.86	5.628	291.37	6.034
170.37	5.638	292.26	6.054
175.58	5.671	297.81	6.097
Series 2, Calorimeter 1, 6-25-31			
15.34	0.153		
21.60	0.481		
24.48	0.677		
28.50	0.997		
33.00	1.402		
38.63	1.883		
43.83	2.299		
49.00	2.712		
53.74	3.052		
58.85	3.357		
Series 3, Calorimeter 1, 7-3-31			
16.19	0.191		
19.04	0.323		
21.80	0.496		
Series 4, Calorimeter 2, 4-7-35			
15.03	0.172		
17.06	.259		
19.30	.370		
22.00	.542		
24.98	.753		
Series 5, Calorimeter 2, 5-23-35			
15.07	.169		
17.07	.248		
18.93	.348		
Series 6, Calorimeter 1, 7-12-35			
14.43	.152		
17.09	.260		
20.11	.421		
Series 7, Calorimeter 3, 3-31-39			
16.99	.245		
18.99	.354		
21.28	.482		
23.78	.653		
27.29	.918		
31.32	1.248		
35.56	1.639		
40.07	2.016		
45.16	2.414		
49.80	2.758		
Series 8, Calorimeter 3, 5-27-39			
14.22	0.134		
15.85	.172^a		
18.23	.306		
21.69	.511		
25.27	.759		
28.61	1.024		
Sample melted and recrystallized 6-14-39 to 6-17-39			
Series 9, Calorimeter 3, 6-24-39			
14.64	.143		
16.15	.201		
18.49	.321		
21.90	.523		
25.93	.816		

[a] It is possible that this result should be increased by 10% due to a one minute error in timing the energy input.

Heat capacity measurements from 15–300°K. were made in the calorimeter described in the previous paper.[1]

Since the heat capacities of silver and lead do not decrease to very low values at 15°K. these substances were placed in another calorimeter so that they could be measured at lower temperatures. The arrangement did not prove very satisfactory, due to difficulty in removing adsorbed helium from silk and bakelite covered wire in the insulating vacuum space, so we will omit a description of the second calorimeter. At the temperatures of liquid hydrogen the second calorimeter was quite satisfactory and the data given

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(1) Giauque and Meads, This Journal, **63**, 1897 (1941).

for silver in Series 4 and 5 of Table I were obtained with this apparatus. All of the heat capacity data on silver, obtained with calorimeters 1 and 2, are given in Table I which also includes data obtained with calorimeter number 3 which will be mentioned later. One calorie was taken as 4.1833 international joules.

The results of Series 4 and 5 are about 10% higher in the range 15–25°K., than those obtained in Series 2 and 3 with the first calorimeter. When this was noted it was assumed that one of the two calorimeters must be subject to some unknown error. The sample was replaced in the first calorimeter and the results were then found to be in agreement with Series 4 and 5. These data are given as Series 5. A natural assumption was that some error had occurred during Series 2 and 3 and we reëxamined the data of these series hoping to find the source of the discrepancy. Many ways of checking the results were available but no evidence of error could be found. The resistance thermometer had been checked against the vapor pressure of hydrogen and the standard thermocouple also had been found to read correctly at these temperatures. Comparison of the resistance of the thermometer-heater as obtained from current–voltage observations during energy input and when used as a thermometer eliminated possible error in energy measurement. The corrections due to heat transfer from the surroundings were normal. At this point it was necessary to postpone further work and the data were withheld from publication pending further investigation.

Series 2 and 3 had been made forty and forty-eight days, respectively, after the preparation of the single crystal and it was thought that perhaps some time effect had been responsible for the different results obtained four years later in series 4 and 5. To check this point the sample which had stood for eight years was placed in a third calorimeter. The results, which are given as Series 7 and 8, agreed with Series 4, 5 and 6. This was not unexpected.

The metal was then re-melted in a vacuum (an atmosphere of nitrogen had been used in the previous crystallization) and a single crystal prepared as before. The solidification and cooling required three days. Series 9 was measured seven days after the preparation of the new crystal and agreed with Series 4, 5, 6, 7 and 8 seemingly eliminating time effect as an explanation of the low results in Series 2 and 3. The measurements of all series contain a continuous record of observations from the lowest to the highest temperatures. Thus a discrepancy of about 10% between 15 and 25°K. represents a completely measured 10% difference in heat content over this interval. Since an independent check of energy input was available, as mentioned above, it would require a 1° error in the temperature interval to explain the effect. However, all temperatures were measured with both a thermocouple and resistance thermometer which agreed exceedingly well and were, moreover, then compared with the vapor pressure of hydrogen while they remained in place on the calorimeter which still contained the sample and had not been disturbed in any way. Series 2 and 3 agree very well with each other and above 25°K. the data gradually approach coincidence with the later series.

The data of Series 4–9 are taken as representing the heat capacity of silver in selecting the values taken from a smooth curve and in calculating the entropy.

TABLE II

HEAT CAPACITY OF LEAD

Atomic weight 207; 0°C. = 273.10°K.

T, °K.	C_p, cal. deg.$^{-1}$ g.-atom^{-1}
Series 1	
64.54	5.446
69.52	5.534
74.84	5.603
80.39	5.656
86.13	5.718
90.96	5.740
96.00	5.791
101.77	5.872
107.54	5.897
113.39	5.931
120.37	5.933
127.72	5.956
135.26	5.994
143.40	6.038
151.63	6.046
160.03	6.069
167.97	6.088
176.40	6.138
184.48	6.148
192.61	6.139
200.75	6.164
209.04	6.189
217.61	6.230
226.00	6.232
234.99	6.276
244.01	6.283
252.58	6.327
260.98	6.342
269.44	6.355
277.89	6.387
284.66	6.412
292.60	6.377
299.91	6.418
Series 2	
15.74	1.800
19.06	2.468
23.08	3.092
27.78	3.689
32.85	4.215
37.79	4.559
42.87	4.810
48.23	5.046
53.42	5.235
58.85	5.337
Series 3	
15.47	1.735
18.77	2.411
22.74	3.039
27.06	3.599
Series 4	
14.16	1.561
16.95	2.150
20.11	2.667
23.62	3.271

The results agree quite well with those of Eucken, Clusius and Woiteneck[2] who measured the heat capacity of silver from 11 to 205°K. Their results are about 1% lower than the present observations over most of the range.

The results on the heat capacity of lead are given in Table II. Series 1, 2 and 3 were made in calorimeter 1. Series 4 and 5 were made in calorimeter 2.

The earlier data on the heat capacity of lead have been summarized by Rodebush and Rodebush.[3] The smoothed data given in their summary are about 1.5% high at 20°K., approach agreement with the present results near 100°K. and then cross the present curve, becoming 1 to 2% low between 200 and 300°K.

TABLE III

THERMODYNAMIC PROPERTIES OF SILVER

Cal. deg.$^{-1}$ g.-atom^{-1}, 0°C. = 273.10°K., atomic wt. 107.880

T, °K.	C_p	C_v	C_v/C_v Debye	S	$(H^0 - H^0_0)/T$	$-(F^0 - H^0_0)/T$
15	0.160	0.160	0.98	0.054	0.040	0.014
20	.410	.410	1.08	.131	.097	.034
25	.747	.747	1.063	.256	.192	.064
30	1.141	1.140	1.032	.427	.317	.110
35	1.580	1.578	1.023	.635	.465	.170
40	2.005	2.001	1.010	.874	.632	.242
45	2.399	2.393	0.998	1.134	.807	.327
50	2.784	2.776	.999	1.407	.985	.422
60	3.420	3.405	.996	1.973	1.341	.632
70	3.904	3.881	.992	2.539	1.674	.865
80	4.277	4.245	.990	3.086	1.977	1.109
90	4.573	4.532	.990	3.608	2.250	1.358
100	4.820	4.769	.993	4.103	2.495	1.608
110	5.010	4.950	.994	4.570	2.715	1.855
120	5.162	5.092	.995	5.013	2.913	2.100
130	5.289	5.210	.996	5.431	3.091	2.340
140	5.399	5.310	.997	5.828	3.252	2.576
150	5.490	5.391	.998	6.203	3.398	2.805
160	5.569	5.461	.999	6.559	3.531	3.028
170	5.644	5.526	1.001	6.899	3.653	3.246
180	5.712	5.584	1.004	7.224	3.766	3.458
190	5.757	5.620	1.003	7.533	3.869	3.664
200	5.800	5.653	1.003	7.830	3.965	3.865
210	5.837	5.681	1.003	8.114	4.053	4.061
220	5.873	5.708	1.003	8.387	4.135	4.252
230	5.911	5.736	1.004	8.648	4.211	4.437
240	5.950	5.765	1.006	8.901	4.283	4.618
250	5.989	5.793	1.007	9.144	4.351	4.793
260	6.025	5.819	1.009	9.380	4.414	4.966
270	6.050	5.835	1.010	9.607	4.474	5.133
280	6.068	5.843	1.009	9.828	4.531	5.297
290	6.080	5.846	1.007	10.042	4.584	5.458
298.1	6.092	5.851	1.007	10.206	4.605	5.584
300	6.095	5.852	1.007	10.248	4.634	5.614

Bronson and Wilson[4] have measured the heat capacity of lead from −80 to 120°C. Their results are about 2% lower at 200° and 1% lower at 300°K. than those obtained in the present measurements.

In Tables III and IV heat capacity values taken from smooth curves through the data are presented. The values for the heat capacity at constant volume, C_v, given in column 3 were obtained by means of the empirical equation

$$C_p - C_v = ATC_p^2$$

The constant A was evaluated at ordinary temperatures by means of the thermodynamic equation

$$C_p - C_v = \alpha^2 VT/\beta$$

as in the previous paper.[1]

The values of A used were

Silver: $A = 2.18 \times 10^{-5}$ g.-atom cal.$^{-1}$
Lead: $A = 3.45 \times 10^{-5}$ g.-atom cal.$^{-1}$

TABLE IV

THERMODYNAMIC PROPERTIES OF LEAD

Cal. deg.$^{-1}$ g.-atom^{-1}, 0°C. = 273.10°K., atomic wt. 207.22

T, °K.	C_p	C_v	C_v/C_v Debye	S	$(H^0 - H^0_0)/T$	$-(F^0 - H^0_0)/T$
15	1.728	1.727	1.098	0.705	0.514	0.191
20	2.632	2.627	1.025	1.341	0.940	.401
25	3.360	3.350	0.999	2.002	1.353	.649
30	3.943	3.927	.997	2.669	1.738	.931
35	4.369	4.346	.995	3.311	2.085	1.226
40	4.677	4.647	.993	3.916	2.391	1.525
45	4.910	4.873	.992	4.479	2.659	1.820
50	5.100	5.055	.993	5.007	2.894	2.113
60	5.361	5.301	.993	5.962	3.285	2.677
70	5.536	5.462	.994	6.802	3.595	3.207
80	5.661	5.573	.996	7.550	3.846	3.704
90	5.758	5.655	.997	8.223	4.053	4.170
100	5.838	5.720	.999	8.834	4.228	4.606
110	5.900	5.768	1.001	9.393	4.377	5.016
120	5.938	5.792	0.999	9.908	4.506	5.402
130	5.971	5.811	.999	10.385	4.617	5.768
140	6.007	5.833	.999	10.829	4.715	6.114
150	6.039	5.850	.999	11.244	4.802	6.442
160	6.070	5.863	.999	11.635	4.880	6.755
170	6.106	5.887	1.002	12.004	4.951	7.053
180	6.135	5.901	1.003	12.354	5.016	5.338
190	6.159	5.910	1.003	12.686	5.076	7.610
200	6.183	5.919	1.003	13.003	5.131	7.872
210	6.207	5.927	1.004	13.305	5.181	8.124
220	6.229	5.934	1.004	13.594	5.228	8.366
230	6.250	5.940	1.004	13.872	5.274	8.598
240	6.270	5.944	1.004	14.138	5.313	8.825
250	6.301	5.958	1.006	14.395	5.352	9.043
260	6.331	5.971	1.008	14.643	5.389	9.254
270	6.363	5.985	1.010	14.882	5.425	9.457
280	6.380	5.986	1.010	15.114	5.459	9.655
290	6.398	5.987	1.009	15.338	5.491	9.847
298.1	6.414	5.990	1.010	15.514	5.515	9.999
300	6.418	5.991	1.010	15.555	5.521	10.033

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(2) Eucken, Clusius and Woiteneck, *Z. anorg. allgem. Chem.*, **203**, 39 (1931).

(3) Rodebush and Rodebush, "I. C. T.," Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1929, p. 85.

(4) Bronson and Wilson, *Can. J. Research*, **14A**, 181 (1936).

In the fourth columns of Tables III and IV the ratio of the C_v to the C_v calculated from the Debye equation has been given.

The characteristic temperatures were calculated from the temperature where C_v reached the value $^3/_2\ R = 2.980$ cal. deg.$^{-1}$ g.-atom^{-1}. For silver this temperature was found to be 52.9°K. and the corresponding $\theta = 212.7$.

For lead $T = 22.45$°K. and $\theta = 9.3$.

As we have explained in the previous paper, it is not our purpose to compare our results with the Debye function, although this is the best way of doing this, but rather to use it as an idealized reference equation to facilitate the comparison of the several metals with each other.

Aluminum and copper, discussed in the previous paper,[1] and silver and lead each has a face centered cubic structure. From the comparisons of C_v/C_v Debye it may be seen that the deviations of all four substances have the same typical characteristics.

It is clearly evident from the C_v/C_v (Debye) ratios at the lower temperatures in Tables III and IV that the *a priori* probabilities or number of degrees of freedom associated with the various fundamental frequencies are not those corresponding to a structureless solid as the Debye equation assumes. That this would be found to be the case has recently become evident from the calculations of Blackman[5] and particularly from the theoretical investigation of Fine,[6] who has made a calculation of the heat capacity of tungsten using only the elastic properties. This substance crystallizes in the body-centered cubic form which complicates comparison with the present case but the same general features are evident at low temperatures where quantum differences are able to stand out. As in the present case the heat capacity at the lower temperatures decreases to values considerably below those which would be calculated from a Debye θ, which satisfies the experimental results at higher temperatures. There is of course no question but that the Debye curve correctly represents the contribution to the heat capacity due to vibrations of the lattice at very low temperatures but the θ which will represent the limiting behavior is considerably greater than the value which best represents the upper portion of a heat capacity curve. This greater value of the Debye θ should correspond to that derived from the elastic properties of the material.

We note that Dr. Fine[6] indicates an interest in extending his calculations to crystals of the face centered cubic type such as we have investigated and it is hoped that the present data will assist in determining the characteristics of the fundamental frequencies involved.

Although C_v/C_v (Debye) values for the four substances all have the same general characteristics the maxima which occur in the neighborhood of $T/\theta = 0.1$ are higher and appear at lower temperatures as the value of the characteristic θ increases.

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Summary

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

Values of the thermodynamic quantities S, $(H-H_0^0)/T$ and $(F-H_0^0)/T$ have been tabulated to 300° K.

The entropies of silver and lead were found to be 10.21 and 15.51 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.1° K. These entropy values are the ones to be used in ordinary thermodynamic calculations and therefore do not include nuclear spin or isotopic contributions to the absolute entropy.

Heat capacity data for aluminum, copper, silver and lead, all of which form face centered cubic crystals are compared by means of the Debye equation used as an idealized limiting case.

It has been found that the values of C_v/C_v (Debye) pass through a maximum in the temperature region near $T/\theta = 0.1$, however, the maxima are higher and occur at lower temperatures for the smaller values of the characteristic temperature θ when this quantity is determined by means of the temperature where $C_v = {}^3/_2\ R$.

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(5) Blackman, *Proc. Roy. Soc.* (London), **A148**, 365, 384 (1935); **149**, 117, 126 (1935).

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