LA-2307
INSTRUMENTS
(TID-4500, 14th edition)

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: March 1959

REPORT DISTRIBUTED: June 25, 1959

**HEAT CAPACITY OF COPPER BELOW 300°K,
A TEST OF TWO CALORIMETER DESIGNS**

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Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

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ABSTRACT

Two designs of adiabatic calorimeters, in which the surroundings follow the temperature of a test specimen at all times from the lowest temperature achieved by cooling up to room temperature, are described.

Values for the heat capacity of oxygen-free, high conductivity copper are given in order to show the reliability to be expected from determinations of heat capacity of elements in which the self-heating by radioactive disintegration is appreciable and can be used as the sole source of heating. Equations based on least-squares analysis of data are listed for the OFHC copper.

The methods of numerical integration used for thermodynamic properties are described and values of entropy and enthalpy of copper at 298.15°K are shown.

ACKNOWLEDGMENTS

The author desires to thank the following individuals and groups of the Los Alamos Scientific Laboratory for their assistance:

CMB Shops for machining of the metal parts making up the various assemblies in the described apparatus;

CMB-7 for alterations made in the controller-recorder units and for conversion of a standard Brown recorder into a 40-step recorder;

R. H. Sherman of CMF-9 for calibrated thermocouple wires and temperature tables;

CMB-1 for chemical analyses of the OFHC copper and copper-nickel alloy wire;

C. E. Olsen and R. B. Gibney of CMF-13 for consultations on design, in transferring liquefied gases, and for taking readings of current and voltage during specific heat runs;

L. S. Richardson (now of Westinghouse Electric Corporation), who set up the original IBM 704 codes; and W. V. Green of CMF-13 for teaching the writer Fortran Coding;

E. C. Kerr of CMF-9 for discussions on helium calorimeter designs.

1. INTRODUCTION

The determination of the heat capacity of copper was undertaken primarily as a test of the accuracy and reproducibility of two types of specific heat calorimeters designed for measurement of the heat capacity of plutonium.

The temperature of a thermally isolated specimen of plutonium rises as a result of self-heating. The rate of rise of temperature is dependent upon the variation of specific heat with temperature, since the heat output per gram must be assumed to be constant. The design of an adiabatic calorimeter, in which the surroundings would follow the temperature of a plutonium specimen at all times, from the lowest temperature achieved by cooling to room temperature, was undertaken.

Because of the very rapid temperature response of a tubular resistance heater, its thin wall construction, and low mass, a design incorporating a tube heater as an adiabatic shield for a test specimen seemed very desirable. The tube heater calorimeter first constructed was really a prototype that was used to prove the feasibility of such a system at high temperatures. It was also satisfactory down to temperatures obtained by cooling with liquid hydrogen, but it was too massive for cooling with liquid helium. For this reason a second calorimeter was built using all of the basic components and controllers of the original tube heater calorimeter but minimizing masses of metals.

The results given in this paper for oxygen-free, high conductivity (OFHC) copper should be proof enough of the reliability to be expected from determinations of the heat capacity of any metal with these two types of calorimeter.

2. EXPERIMENTAL DETAILS

2.1 Apparatus

With radiation losses minimized by adiabatic shields, the two sets of apparatus were assembled in such a manner that heat leaks along thermocouple wires, etc., would not influence the rate of temperature rise of the test specimen.

The schematic design of the tube heater calorimeter is shown in Fig. 1. Thermocouple wires, current leads, and potential drop measuring leads from the test specimen were passed through double spiral grooves in the "temperature-equalizing block." These leads then were wrapped around a copper spool which was an integral part of the outer brass can. All this was done to prevent heat leaks to the test specimen. From the copper spool the same leads were then passed through a short length of copper tubing and finally a section of Inconel tubing. These sections of tubing (electrically grounded) acted as electrical shielding from the relatively high currents required by the tube furnace. The power to the thin wall Inconel heater tube, which was used as an adiabatic shield, was supplied by a high current, low voltage transformer.

The basic parts of the tube heater design were thus the test specimen (wound with a copper-nickel alloy heater), the temperature-equalizing block, the tube heater, a silver radiation shield, and an outer brass vacuum jacket wound with heater wire. Cooling of specimens involved helium as an exchange gas and liquid nitrogen or liquid hydrogen.

The second apparatus, shown in Fig. 2, was designed to be light in weight and suitable for cooling of specimens by direct contact with liquid helium or any other liquefied gas. The parts of the second apparatus were machined from copper because of its excellent thermal conductivity at low temperatures. A lead sheet was wrapped around the bottom section of the adiabatic shield in order to have a material with

Fig. 1. Tube heater design of calorimeter.

Fig. 2. Liquid helium calorimeter.

high specific heat present at the lowest temperature ($\sim 4^{\circ}\text{K}$), so that heat leaks along the fine heater and thermocouple wires would not cause the temperature of the calorimeter to rise faster than that of the specimen. Since a liquefied gas was to be used to cool the test specimen by direct contact, its removal was necessary before commencement of any run. A transfer tube arrangement is shown in Fig. 2. Not shown in the figure is the outer strip-silvered dewar and standard brass cryostat can with windows.

Power to the heaters for the second apparatus was initially supplied by battery circuits. In the later runs, commercially available Transpac power supplies were used in place of batteries.

To prevent contamination of apparatus by oxides of plutonium, it would be necessary to "can" the plutonium specimen for which the heat capacity was to be measured. Since the heat capacity of OFHC copper was being determined as a test of the apparatus, it was thought that OFHC copper would also be an excellent material in which to contain plutonium specimens. The simple spring-loaded copper can shown surrounding the copper test specimen (in Figs. 1 and 2) was added in order to prove that light spring loading of thermocouples and spring loading of an outer jacket would still allow reproducible and accurate determinations of specific heat values.

2.2 Controllers and Recorders

Three recording proportional controllers were used with each of the calorimeters. These were standard Brown proportional controllers with electropulse relays. Two of the instruments had ranges of 1 mv full scale, and the third had a range of 0.5 mv full scale. The control points of the three recorder-controllers were biased at mid-scale by auxiliary circuits.

Differential thermocouples were used for temperature matching. The tube heater calorimeter was equipped with copper vs constantan differential thermocouples and temperature-indicating thermocouples.

The thermocouple wires used with the liquid helium apparatus were cobalt-gold alloy vs copper. Thermocouple wires of both types were calibrated by the National Bureau of Standards Laboratories in Boulder, Colorado. In addition, the wires were checked in boiling liquid helium, hydrogen, and nitrogen by the writer. As a further check of the accuracy of measured temperatures in the range between 48°K and 300°K, the wires (both types of thermocouples) were compared with copper-constantan thermocouples supplied by R. H. Sherman. The latter thermocouple wires had been checked by Sherman against a calibrated resistance thermometer over the entire temperature range of 4°K to 300°K. The particular thermocouple wires (cobalt-gold alloy vs copper) used in the liquid helium calorimeter had an emf of 10.305 mv with junctions at the ice point and liquid helium, at Los Alamos normal pressure.

The recorder-controllers and differential thermocouple were utilized as follows: One controller maintained the temperature of the temperature-equalizing block at the temperature of the specimen; another maintained the adiabatic shield at the temperature of the temperature-equalizing block; the third maintained the top copper block assembly and the brass vacuum jacket at the temperature of the adiabatic shield. (The third controller was used with the liquid helium apparatus to maintain the top adiabatic shield heater and copper block head unit at the temperature of the temperature-equalizing block.)

The record of time and temperature was made on a Brown recorder which had a scale of -0.1 to +1.0 mv. A system of mercury switches, stepping relays, precision resistors, and stable d.c. supply gave a range of 40 mv in 1 mv steps to this instrument. This recorder had the ability to follow temperature up or down. Since not every resistor was hand picked to have exactly the same resistance, it was necessary to manually feed a known emf into the recorder on each scale. Only one recorded point was necessary on any one of the 40 possible scales, but at least four or five points were recorded in order to show any scale

drift with time. The record of time during a day's run was checked against the National Bureau of Standards radio time signals.

2.3 Experimental Procedure

Tube Heater Calorimeter

Helium exchange gas was added to the previously evacuated system to a pressure of approximately 10 mm Hg. Liquefied gas was added to the surrounding dewar and the temperature recorder was turned on when the specimen had been cooled to what appeared to be the minimum temperature attainable. Recorder-controllers were turned on and adjusted. The specimen heater was turned on with sufficient power to cause the copper specimen to rise in temperature (in vacuum) at a previously determined rate comparable to that of a plutonium specimen. Shield heaters were finally turned on and the evacuation of the helium exchange gas started.

Current and voltage readings for the copper specimen heater were taken periodically during a run. These readings were taken on separate Rubicon potentiometers, and the time at which simultaneous readings of these values were taken was read from 1/100 min interval timers.

Time was recorded on the emf chart at frequent intervals and the indicated time was checked against NBS time signals. As pointed out before, known emf pips were placed on the temperature record (at approximately 0.25 mv intervals).

Temperature matching of various parts of the calorimeter was checked frequently by throwing reversing switches in the differential thermocouple circuits. Currents to the various heaters (other than for the specimen heater) were varied during the runs in order to keep the recorded control line as nearly straight as possible on each of the three controller-recorders.

At the end of a day's run, the recorder paper was removed and the record of time and corrected emf was tabulated in a bound notebook. The input watts supplied to the specimen as the run progressed were calculated and recorded. Rate of rise of temperature over short time

intervals was calculated, as well as the average temperature of the interval.

The copper and nickel in the alloy heater wire were assumed to obey Kopp's rule. The copper weight (in the alloy wire) was added to the weight of the copper specimen, and a correction for the small amount of nickel present in the alloy heater wire was applied to the calculated specific heat.

Liquid Helium Calorimeter

Since liquefied gases were to be added directly to the space surrounding the test specimen, it was necessary to take precautions to prevent condensation of moisture on the specimen and inner walls of the dewar during the transfer. This was done by maintaining a slight overpressure of dried helium gas inside the dewar while transferring liquefied gas into it.

Liquid nitrogen (fresh from the liquefier) was first introduced, to cool the specimen and its surroundings. The excess was removed by increasing the pressure of dry helium and forcing it out through the inner transfer tube arrangement. After removal of most of the liquid nitrogen in this way, the vacuum space was evacuated until pressure gauges indicated that the remaining nitrogen liquid had been boiled away.

Liquid helium was then transferred into the dewar to a depth sufficient to just cover the specimen and its surrounding metal shields. After a holding time of 15 to 30 min, the copper specimen heater was turned on, and removal of the excess liquid helium was started. It was removed by evacuating a large manifold to which the inner helium transfer tube was connected.

The temperature recorder was started at the initiation of the liquid helium transfer, as were the three recording proportional controllers. As soon as the quieting of large vacuum pumps indicated that liquid helium removal was complete and the temperature of the test specimen started to rise, switches for heaters on the shields, etc.,

were thrown to the "on" position.

The remainder of the procedure was the same as that described for the tube heater apparatus.

It should be pointed out that below 20°K, the heat capacity of copper is so low that the power supplied to the specimen heater was of the order of milliwatts. The power to the heater was increased twice in covering the range of 4°K to 300°K.

All calculations of the values of specific heat of copper, for all runs in both designs of apparatus, were made with a hand-operated calculator. These calculations were tedious and time consuming. Fortunately, by the time measurements of the specific heat of plutonium were progressing satisfactorily, all calculations had been coded for solution by an IBM 704 and answers for C_p , S, H, and F were available at the end of the second day after a run.

3. SPECIMEN DESCRIPTION

The copper test specimen upon which determinations were made was machined from what was classified as dead-soft annealed, oxygen-free, high conductivity copper. Chemical analysis indicated 99.96% copper, with impurities as indicated in Table I.

TABLE I.
IMPURITIES OF OFHC COPPER BY SPECTROGRAPHIC ANALYSIS

Element	Impurity, %
Mg	<0.001
Si	<0.001
Ca	<0.001
Fe	<0.001
Ni	<0.001
Pb	<0.001
Bi	<0.001
Ag	0.001 to 0.01
Sb	0.001 to 0.01
Other	Not detectible

The analysis of the copper-nickel alloy heater wire indicated the composition to be as follows: Cu, 53.8%; Co, 0.04%; Mn, 0.30%; Ni, remainder.

4. EXPERIMENTAL RESULTS

The results of measurements of specific heat of copper, obtained with both designs of apparatus described above, were submitted for least-squares analysis utilizing the IBM 704 Calculator. It was found that one equation would not satisfactorily cover the entire range from 4°K to 300°K. The most desirable equations for the data obtained with each apparatus design are given below for limited temperature ranges.

The tube heater apparatus allowed for cooling of the copper specimen only by liquid hydrogen and helium exchange gas. The copper was not cooled below 30°K with the specimen heater "on," and correct operation of controllers was not achieved below 35.74°K. For this reason the data on copper heat capacity obtained with this apparatus begin at this temperature.

4.1 Equations Based on Tube Heater Data

The equations for the heat capacity of copper determined by least-squares analysis of the data from the tube heater apparatus were:

Temperature Range: 35.74°K to 88°K

$$C_p = A + BT + CT^2 + DT^3$$

$$A = -1.5557453$$

$$B = 6.1529893 \times 10^{-2}$$

$$C = 8.8340380 \times 10^{-5}$$

$$D = -1.5711210 \times 10^{-6}$$

$$\sigma = 0.050 \text{ (i.e., standard deviation)}$$

Temperature Range: 88°K to 300°K

$$C_p = A + BT + CT^2 + DT^3 + ET^4$$

$$A = -2.7963454$$

$$B = 1.1538410 \times 10^{-1}$$

$$C = -6.3396582 \times 10^{-4}$$

$$D = 1.6247728 \times 10^{-6}$$

$$E = -1.5733022 \times 10^{-9}$$

$$\sigma = 0.075$$

4.2 Equations Based on Liquid Helium Data

The equations for the heat capacity of copper determined by least-squares analysis of the data from the liquid helium apparatus were:

Temperature Range: 4°K to 27°K

$$\begin{aligned}C_p &= AT + BT^3 \\A &= 1.59997056 \times 10^{-4} \\B &= 1.30379227 \times 10^{-5} \\\sigma &= 0.0066\end{aligned}$$

Temperature Range: 36°K to 123°K

$$\begin{aligned}C_p &= 63.54 \left[A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6 \right] \\A &= 7.8830334 \times 10^{-3} \\B &= -1.3599803 \times 10^{-3} \\C &= 6.0591839 \times 10^{-5} \\D &= -7.1898676 \times 10^{-7} \\E &= 3.9676715 \times 10^{-9} \\F &= -1.0482111 \times 10^{-11} \\G &= 1.0676381 \times 10^{-14} \\\sigma &= 0.0020\end{aligned}$$

Temperature Range: 144°K to 255°K

$$\begin{aligned}C_p &= 63.54 \left[A + BT + CT^2 + DT^3 \right] \\A &= -2.3957066 \times 10^{-2} \\B &= 1.2057836 \times 10^{-3} \\C &= -4.3940431 \times 10^{-6} \\D &= 5.5223524 \times 10^{-9} \\\sigma &= 0.0022\end{aligned}$$

Above 255°K there were not enough points, and the curve "tailed off."

As pointed out above, the least-squares analysis of all heat capacity data obtained below 21.08°K yielded the equation

$$C_p = AT + BT^3$$

where

$$A = 1.6000 \times 10^{-4}$$

$$B = 1.3038 \times 10^{-5} \text{ (approximately)}$$

The term AT is equivalent to the γT of the literature, which is associated with the electronic contribution to the heat capacity. Therefore γ has the value of 1.6×10^{-4} . This value of γ yields a value for the energy density of states of 0.14 state per atom per ev. The coefficient of T^3 (i.e., B) gives a calculated value for θ_D (Debye characteristic temperature) of 329°K.

The values for the heat capacity of copper, as a function of temperature, were needed in making corrections for the copper involved in subsequent heat capacity measurements on plutonium. Before a least-squares analysis of copper was made, all experimentally determined values were considered and an arbitrarily chosen set of best values was tabulated. This tabulation is included (column 3) in Table II, which lists heat capacity values of the OFHC copper at temperatures between 0°K and 298.15°K. The values given in columns 2 and 4 of Table II were obtained by interpolation of least-squared experimental data, with an IBM 704 routine.

The heat capacity data for copper were used in numerical integration equations to get the values of entropy, enthalpy, and free energy at temperatures between 4°K and 298.15°K. The assumption made in using the equations below was that C_p and entropy at 0°K were zero. Calculations were made with the IBM 704 using the following equations:

$$H(1) = C_p(1) \frac{T(1)}{2}$$

$$S(1) = \frac{C_p(1)}{T(1)} \frac{T(1)}{2}$$

$$F(1) = H(1) - T(1) S(1)$$

The values of the thermodynamic properties were then calculated by

TABLE II
HEAT CAPACITY OF OFHC COPPER BELOW 300°K

Temperature, °K	Heat Capacity (C_p) of Copper, cal/mole/°K		
	Tube Heater Calorimeter	Arbitrarily Chosen Values	Liquid Helium Calorimeter
0	--	0.000	0.000
5	--	0.003	0.002
10	--	0.014	0.015
15	--	0.042	0.047
20	--	0.114	0.108
40	0.946	0.883	0.860
60	2.115	2.075	2.089
80	3.128	3.130	3.159
100	3.870	3.882	3.898
120	4.402	4.379	4.354
140	4.786	4.735	4.722
160	5.060	5.040	5.026
180	5.256	5.271	5.269
200	5.403	5.461	5.440
220	5.519	5.597	5.556
240	5.620	5.684	5.633
260	5.715	5.742	5.696
280	5.805	5.792	5.743
290	5.847	5.815	5.773
298.15	5.881	5.833	5.801

TABLE III
THERMODYNAMIC PROPERTIES OF OFHC COPPER AT ROOM TEMPERATURE (298.15°K)

	S_{298}	$H_{298} - H_0$
Tube heater calorimeter	7.995 ^a	1202.17 ^a
Arbitrarily chosen data	7.966	1202.75
Liquid helium calorimeter	7.946	1198.17

^aAveraged values of S and H from other runs were substituted into summing equations at 35.74°K to yield this value.

summation from the first point as follows, with I running from 2 to n, where n = number of values:

$$\begin{aligned} H(I) &= H(I - 1) + \left\{ [C_p(I) + C_p(I - 1)]/2 [T(I) - T(I - 1)] \right\} \\ S(I) &= S(I - 1) + \left\{ [C_p(I) + C_p(I - 1)]/2 \ln[T(I)/T(I - 1)] \right\} \\ F(I) &= H(I) - T(I) S(I) \end{aligned}$$

It can be seen from these equations that the calculation of H and S involves a trapezoidal rule integration.

The area under one of the C_p vs T curves for copper was also determined using a Simpson rule integration routine with the IBM 704 computer. The quantity $(H_{298} - H_0)$ from the latter integration method agreed with the value from the trapezoidal rule integration to within 2 parts in 12,000.

Values of entropy (S_{298}) and enthalpy ($H_{298} - H_0$) are given in Table III. These were calculated from the data for the heat capacity of copper using the summation equations given above.

5. DISCUSSION OF RESULTS

Although there is a spread in values of C_p at 298.15°K, as shown in Table II, the average of the three agrees very well with published results.* The values of S_{298} and $(H_{298} - H_0)$ also agree very well with literature values.* Summation by a trapezoidal rule, which is the basis of the equations used to calculate S and H, is evidently adequate when temperature intervals are small. Values of γ and θ_D , calculated from experimental values of C_p below 21°K, were very good.

Apparently, then, the accuracy and reproducibility of results to be expected from the two apparatus designs and experimental techniques are satisfactory. An additional copper can with a relatively loose fit did not appear to detract from them. The rate of temperature rise used was 0.4 to 0.7 deg/min, which is similar to that expected of plutonium

*Selected Values for the Thermodynamic Properties of Metals and Alloys, Minerals Research Laboratory, Institute of Engineering Research, University of California, Berkeley, California (1955), page Cu2.

in vacuum. It is believed, therefore, that satisfactory determinations of the heat capacity of plutonium can be made using either apparatus.

The numerical coefficients of the equations of Section 4, giving the heat capacity of copper as a function of temperature over various temperature ranges, were obtained by a least-squares treatment of experimental data, using IBM 704 electronic data processing machines. On an IBM 704, least-squares fitting to a series of points of an equation of any degree up to the sixth requires 1.5 min or less. It was therefore possible to fit to each set of data a series of equations in powers of T up to T^6 , and to evaluate the fit obtained in each case in terms of a standard deviation (σ), which was easily calculated from data given by the 704. The equations given in Section 4 were those which, on the basis of minimum σ , gave the best fit to experimental data over each temperature range.

The data to which these curves were fitted were the pooled results of several runs. Experimental data from any single run were scattered, and to obtain an acceptably smooth curve, it was found necessary to combine the results of a number of runs for each least-squares treatment.