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Atomic Heats of Copper, Silver, and Gold from 1°K to 5°K*

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The atomic heats of copper, silver and gold have been determined in the temperature interval 1.0° to 5.0° K. The measured values can be described adequately by a linear plus a cubic term in temperature. Any deviations from this relationship are explainable in terms of inaccuracies in the presently accepted helium vapor pressure—temperature scale. In fact, it is shown that the temperature scale corrections, necessary to correct the data to the simple law given above, essentially agree with temperature scale corrections suggested by other work. Values of the coefficient of the linear term (electron heat capacity) and the Debye characteristic temperature have been derived and compared with several indirect determinations, as well as with other calorimetric data, where possible. The values of the electronic heat capacity determined in the work are consistently lower than those from previous work on copper and silver.

INTRODUCTION

MEASUREMENTS[1] of the atomic heat of the noble metals in the temperature region 1°K to 5°K have been undertaken in order (a) to extend the region in which the atomic heat of gold has been measured; (b) to investigate the anomaly reported in the atomic heat of silver by Keesom and Pearlman[2]; and (c) to repeat with greater accuracy the earlier measurements made on copper and silver by Keesom and Kok[3,4] so as to make possible a comparison of the experimental atomic heats with the theoretical predictions. Our preliminary experiments on these metals have already been reported.[5]

In the temperature region under consideration the atomic heat of these metals can be considered to be composed of two terms, one linear and one cubic in temperature:

$$c=\gamma T+\beta T^3. \qquad (1)$$

The term linear in temperature is due to the conduction electrons and is related to the density of one-electron energy levels[6] by

$$\gamma=\tfrac{1}{3}\pi^2k^2\eta(\zeta), \qquad (2)$$

where k is the Boltzman constant, $\eta(\epsilon)$ is the number of one electron states per unit energy at the energy ϵ, and ζ is the energy at the top of the Fermi distribution. Buckingham and Shafroth[7] have pointed out that the interaction between electrons and lattice may cause a modification of the density of electron states at low temperatures. This would change the temperature dependence and magnitude of the electronic heat capacity. The term in Eq. (1) that is cubic in temperature is the low-temperature approximation to the lattice heat capacity of a solid.[8] The coefficient, β, is related to the Debye characteristic temperature, Θ, by

$$\beta=(12/5)\pi^4R/\Theta^3, \qquad (3)$$

where R is the molar gas constant. At *sufficiently* low temperatures it is expected that the Debye approximation will hold; but it is not known that the interval 1°K to 5°K is sufficiently low for these metals.[9] In the temperature region where the Debye approximation is valid, Θ should be simply related to the elastic constants of the material. Thus, at $T=0$°K it is expected that the Θ calculated from elastic constants will agree with that determined from heat capacity.

In order to be able to make the separation of the two terms in Eq. (1), and to compare these terms with the theory, it is necessary to obtain an accuracy of measurement which is not characteristic of the earlier work in this field. In the present work, the aim has been to maintain fractional errors in the determinations of atomic heat at less than 1 percent.

EXPERIMENTAL

In Fig. 1 is shown schematically the low-temperature portion of the apparatus, most of the details of which are given in the legend. The thermometer, a carbon resistor,[10] whose plastic insulation has been ground off,

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[1] Westinghouse Research Report No. 60-94466-5-R1 gives, in addition to the material presented in this paper, schematic drawings of the electrical circuits and tables of calibration and heat capacity data. This report is available on request.

[2] P. H. Keesom and N. Pearlman, Phys. Rev. **88**, 140 (1952).

[3] J. A. Kok and W. H. Keesom, Leiden Comm. No. 245a.

[4] W. H. Keesom and J. A. Kok, Leiden Comm. Nos. 219d and 232d.

[5] Corak, Garfunkel, and Wexler, *Third International Conference on Low Temperature Physics* (Rice Institute, Houston, 1953).

[6] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), p. 144.

[7] M. J. Buckingham and M. R. Shafroth, Proc. Phys. Soc. (London) **A67**, 828 (1954).

[8] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), pp. 133–141.

[9] See reference 8, pp. 141–142.

[10] The properties of carbon resistors used as thermometers at low temperatures have been discussed by J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

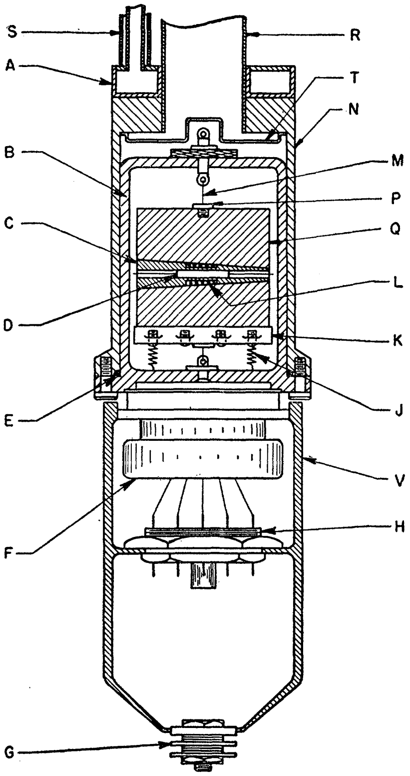

FIG. 1. Calorimeter. *A*, bulb of vapor pressure thermometer; *S*, vacuum jacketed tube to the vapor pressure thermometer; *N*, vacuum tight outer brass container; *R*, pumping tube; *T*, radiation shield; *B*, brass yoke; *Q*, sample; *M*, nylon thread; *P*, brass screws; *K*, beryllium-copper support ring; *J*, thermometer and heater leads; *C*, beryllium-copper tapered plug; *D*, carbon resistance thermometer; *L*, manganin resistance heater; *E*, gold "O" ring; *F*, wire-glass vacuum seal; *H*, coupling plug; *G*, bath heater; *V*, plastic holder.

is lacquered into the plug. Wound on the plug and lacquered in place is the heater, about 2000 ohms of 0.001-in. manganin wire. The ring, the plug with heater and thermometer, and the brass screws make up the addenda whose heat capacity must be subtracted from a measured heat capacity in order to obtain the heat capacity of the sample. The lead-in wires are 0.003-in. manganin wire. There are two current and two potential leads for the heater and for the resistance thermometer. The resistance of the current leads to the heater is approximately 5 ohms each; that of each of the other lead-in wires is about 35 ohms. The gold "O" ring[11] makes the vacuum seal between the brass yoke and the outer container.

In addition to the radiation shield shown in Fig. 1, a trap containing several baffles is located in the high vacuum pumping line just above the sample container. This has been inserted because crude estimates indicate that large amounts of energy (compared with energies involved in a measurement of heat capacity) can be given to the sample from room temperature radiation or from hot gas molecules.

The calorimeter portion of the apparatus is maintained at low temperatures by immersing it in liquid helium in a metal dewar. The dewar holds enough liquid to last for more than 24 hours, making it convenient to extend a heat capacity determination over an interval of several days without warming the apparatus above the temperature of liquid helium. The bath temperature is controlled by a pumping system which makes attainable temperatures down to ~ 1.1°K.

A high-vacuum system is used to isolate the sample after it has been cooled to the bath temperature with helium gas as the exchange medium. The characteristics of this vacuum system have been discussed elsewhere.[12]

To measure both the current through and the potential difference across the carbon resistance a double potentiometer is used. The detector for the potentiometer is a dc amplifier whose output is fed into a Speedomax recorder, so that off-balance potential drops can be recorded as a function of time.

The power to the heater is determined by measurements of both current and potential drop made on a potentiometer. The time of heating is measured by a clock which is started by a relay which also closes the heater current circuit.

The samples are cylinders, 2-in. long by 1-in. diameter. The properties of the samples are given in Table I.

To obtain the heat capacity of a sample, measurements of heater voltage and current, time of heating, and thermometer resistance as a function of time are made. The initial and final temperatures, T_i and T_f, are computed from the resistance measurements, and heat capacity, C, is evaluated by the relationship,

$$C=EIt/(T_f-T_i), \tag{4}$$

where E= heater potential drop, I= heater current, and

TABLE I. Properties of samples.

Sample	Mass (grams)	Purity (%)	Vacuum anneal	Supplier
Cu	221.268	99.999+^{a}	1000°C—3 hr	Amer. Smelt. and Ref. Co.
Cu holder	24.446	99.999+^{a}	1000°C—3 hr	Amer. Smelt. and Ref. Co.
Ag	260.620	99.98^b	700°C—4 hr	Handy and Harmon Co.
Ag holder	17.065	99.98^b	700°C—4 hr	Handy and Harmon Co.
Au	486.38	99.99+^{b}	950°C—4 hr	J. Bishop Co.

[a] Purity given by Smith, Smart, and Phillips, Am. Inst. Mining Met. Engrs. **143**, 272 (1941).
[b] Purity given by supplier.

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[11] Wexler, Corak, and Cunningham, Rev. Sci. Instr. **21**, 259 (1950).
[12] M. P. Garfunkel and A. Wexler, Rev. Sci. Instr. **25**, 170 (1954).

t = time of heating. This is, then, the heat capacity at the average temperature $(T_f+T_i)/2$.

Figure 2 shows two typical recordings of thermometer potential drop as a function of time. The lower part of each curve corresponds to the drift of the temperature of the thermometer before heating; the rapid rise occurs during the heating. The height of the overshoot shows the lead that the temperature of the thermometer has over the temperature of the sample. When the heater power is turned off, the temperature of the thermometer falls back to the sample temperature which then continues to drift as before. As can be seen it is then a simple matter to extrapolate both the drift before and the drift after heating to the center point of the heating period. These extrapolated values of the thermometer potential drop are used to calculate the initial and final resistances. Finally, temperatures are obtained from the resistance-temperature relationship determined from a calibration of the carbon resistance against the vapor pressure of liquid helium.

The results of the measurements give the heat capacity of the particular sample plus the heat capacity of the addenda. Two measurements on silver (silver sample and silver holder) were combined to determine the heat capacity of the addenda. The addenda correction was then available for subtraction from measurements on the copper and gold samples.

A simple calculation of the thermal conductivity of helium gas at liquid helium temperatures shows that (for reasonable assumptions for the accommodation coefficient, i.e., of the order of unity) the pressures necessary for good isolation of the sample are 5×10^{-8} mm of Hg or better. These pressures are easily obtained, and in this experiment have been accurately measured.[12] However, it is only possible to measure the equilibrium pressure in the region of the sample. If, during the heating period helium gas were to be driven from the sample, reducing the insulating vacuum during the time of heating, it would not be detected if it were readsorbed by the walls. This gas would contribute to errors in the measured heat capacity in two ways: it would change the thermal coupling between sample and bath during heating, making extrapolation of drifts incorrect; and it would carry off its heat of adsorption, increasing the apparent value of the heat capacity. In order to investigate the effect of adsorbed gas, an experiment was performed with a copper holder which had approximately the same area as the copper sample but about 1/10 of the mass. The measured heat capacity of this holder was thus very sensitive to the effect of adsorbed gas. The copper holder was coupled to the helium bath with a fine wire, so that it could be cooled to the lowest temperatures without using helium exchange gas. The resulting increased drift rate was tolerated for this experiment. The experiment consisted of making measurements of the heat capacity of this holder, first without using helium gas to cool to the lowest temperature, and then with helium gas. The measurements could only be made down to 1.4°K because the thermal conductivity of the wire coupled with the extraneous heating in the sample maintained a difference of 0.2°K–0.3°K between the sample and the bath.

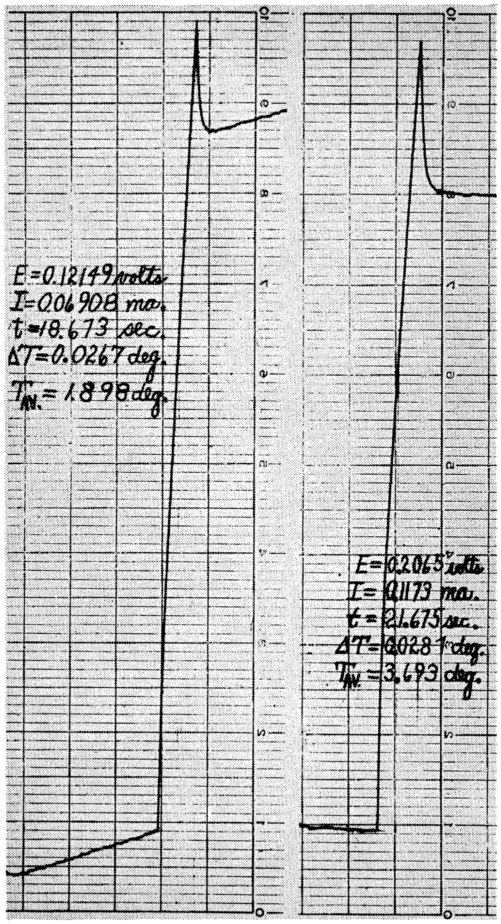

FIG. 2. Typical heating curves.

It was observed that when the sample was at the bath temperature, but thermally isolated from it, the temperature of the sample increased at rates corresponding to heat inputs anywhere from 30 ergs/min to several thousand ergs/min. Some of the sources of this energy may be (a) the dissipation of vibrational energy in either the sample or its suspension and leads, (b) hot gas molecules or room temperature radiation impinging on the sample, (c) electrical pickup being dissipated in the heater or thermometer, and (d) the dissipation of eddy currents induced in the sample by local magnetic fields. It was possible to select for the experimental work, periods of time during which the stray power input from these sources was consistently maintained in the range below 100 ergs/minute. This has been found adequate for the present measurements and, therefore, it was not considered worth the required effort to reduce further this stray energy input.

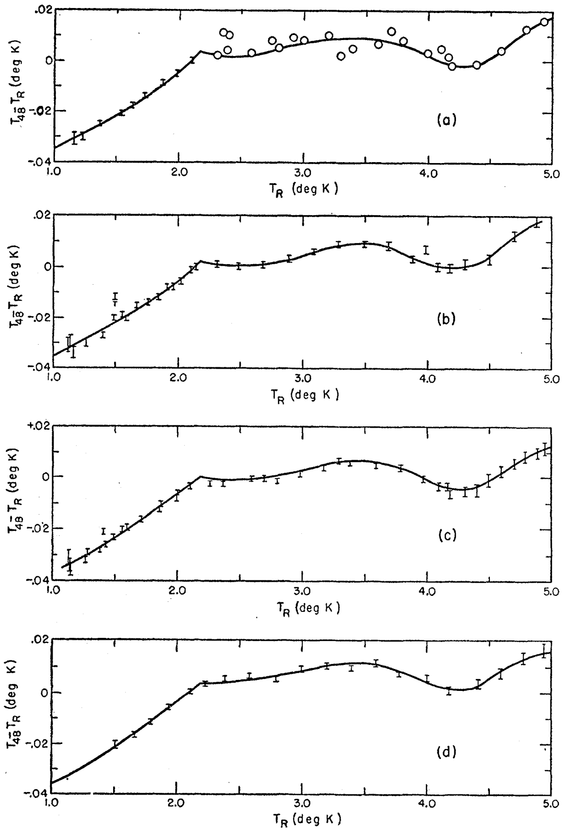

FIG. 3. Thermometer calibration curves (a) in silver holder, (b) in copper sample, (c) in gold sample, (d) in silver sample. The vertical lines in curves (b), (c), (d), and below ~2.2°K in curve (a) indicate the probable error of a measurement.

THERMOMETRY

The resistance thermometer used for all measurements was a $\frac{1}{2}$-watt, 56-ohm, Allen-Bradley carbon composition resistor. The current used in measuring the resistance varied from 0.1 to 5.0 microampere, selected large enough to give adequate accuracy in determining resistance and small enough to give a negligible energy dissipation in the resistor. Calibrations were made as a function of current at several temperatures to find whether there was any current dependence of the resistance. In the range of currents used in this experiment, no current dependence was found.

The resistance thermometer was calibrated against the vapor pressure of liquid helium on the basis of the "agreed" helium vapor pressure-temperature scale of 1948.[13] (Temperatures and quantities which are derived from the temperature scale have a subscript, 48, if the above vapor pressure-temperature scale has been used.) Calibration points were taken at intervals of 0.2°K or less between 2.2°K and 5.0°K, and 0.15°K or less below 2.2°K. A complete calibration was made before each heat capacity experiment, and a few points were repeated after the experiment to check whether the thermometer had changed during the experiment. For calibration, the sample and thermometer were thermally coupled to the bath and vapor pressure thermometer by admitting helium at about 0.030 mm of Hg pressure to the calorimeter at 4.2°K. An experiment showed that this provided adequate coupling: under these helium pressure conditions, a heat input from the heater of several thousand ergs/minute caused a temperature rise of the thermometer of about 0.001°K, while the actual heat flow to the sample from stray sources during calibration was less than 100 ergs/minute.

The temperature of the bath was maintained constant for each calibration point by the regulation of the pressure of helium above the bath by control of the pumping speed. For temperatures above the lambda point of liquid helium, temperatures were always approached from above to avoid the possibility of supercooling the liquid below the surface. Temperature drifts were kept less than 0.0003°K/minute throughout the temperature range, with the exception of the region just above the lambda point where maximum drifts were sometimes as high as 0.001°K/minute.

The helium vapor pressure was measured with manometers of 16-mm precision bore tubing fitted with verniers capable of being read to 0.02 mm. Mercury was used in one manometer for measurements above the helium lambda point, and butyl sebacate in the other manometer for measurements below the lambda point. The butyl sebacate manometer was calibrated by periodic comparisons with the mercury manometer.

In order to calibrate the thermometer, an approximate equation was used which defines a resistance temperature, T_R, and a correction curve was plotted. A convenient two-parameter equation[14] between temperature and resistance, R, which fits remarkably well, is

$$\frac{1}{T_R}=\frac{a^2}{\log R}+b^2\log R+2ab.$$

Two experimental points were used to evaluate the constants a and b, and temperatures, T_R, calculated from the resistance, R, are given throughout the rest of this paper by the equation,

$$\frac{1}{T_R}=\frac{0.73914}{\log R}+0.28552\log R-0.91878, \tag{5}$$

where R is expressed in ohms and T_R in degrees Kelvin. The calibration then consists of obtaining $T_{48}-T_R$ as a function of T_R. These data[1] are plotted in Fig. 3.

Two methods are commonly employed for obtaining the temperature at some point beneath the surface of a liquid helium bath by vapor pressure measurements: measuring the vapor pressure at the surface of the bath

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[13] H. Van Dijk and D. Schoenberg, Nature **164**, 151 (1949).

[14] This equation was suggested to us by J. R. Clement.

and correcting this pressure with the hydrostatic pressure of the column of liquid to the point in question below the surface; or measuring the vapor pressure of helium condensed into a vapor pressure thermometer bulb at the point in question. Both of these methods have been used in these experiments and, therefore, a comparison of the relative reliability of the two methods can be made. The vapor pressure of the cryostat bath was used for the calibration of the thermometer when it was mounted in the silver holder; the vapor pressure thermometer was used for all other calibrations (above the lambda point). In using the bath vapor pressure, corrected for hydrostatic head, for determining temperature, it is assumed that the temperature at any point in the bath is given by the pressure at the surface plus the hydrostatic pressure to that point. This is an unstable temperature distribution in the liquid since the coldest, and therefore most dense, liquid is at the top, and thus, convection currents are set up which try to equalize the temperature throughout the bath to the temperature of the surface. In order to avoid equalization of temperature (since the time constant to reach this condition is unknown), heat was supplied to the bottom of the bath at the rate of 0.040 watt, maintaining vapor-liquid equilibrium throughout the bath, by generating a steady stream of bubbles which rise through the liquid.

As can be seen from the calibration curves of Fig. 3, the scatter of the points, determined from the vapor pressure of the bath [Fig. 3(a)], is many times that determined from the vapor pressure thermometer, [Figs. 3(b), (c), (d)], above the lambda point. In order to locate it exactly, the curve in Fig. 3(a) was assumed to be parallel to the other calibration curves of Fig. 3.

Below the lambda point, the objections to using the vapor pressure of the bath vanish, since the high thermal conductivity of helium II assures equality of temperature throughout the bath. Furthermore, at the lowest temperatures the effect of thermomolecular pressure differences, might be serious if the vapor pressure thermometer were used. Below about 1.4°K this effect was found to cause a difference in pressure reading between the vapor pressure thermometer and the bath. (Because of the superfluidity of helium II, no actual difference in temperature is expected.) For this reason, the vapor pressure of the bath was measured below the lambda point. In the case of the curve in Fig. 3(b) it was necessary to extrapolate the correction curve from 1.4°K down because the original calibration measurements were made with the vapor pressure thermometer, and therefore could not be used.

Uncertainties in temperatures due to the uncertainties in the various measurements comprising a temperature determination are shown by vertical lines on the calibration curves in Figs. 3(b), 3(c), and 3(d). The scatter of the points indicates about the same uncertainty. The correction to the temperature of the thermometer due to the hydrostatic head *difference* between the vapor pressure thermometer and the carbon thermometer has been omitted. This might seem justified in view of the high thermal conductivity of the brass wall of the calorimeter, but a simple calculation shows that even if the wall were of heavy copper a temperature difference of the same magnitude as the hydrostatic head difference could be maintained with a heat flow that is entirely reasonable for this geometry. However, since there is no evidence for this correction from a discontinuity of the calibration curve at the lambda point, the correction has not been made. Undoubtedly, there is a small error introduced by this hydrostatic head difference.

In a heat capacity measurement, errors in the slope of a thermometer calibration curve introduce fractional errors in the heat capacity equal to the slope error. Estimates of the slope error of our calibration curves indicate that they are less than 0.5 percent everywhere except in the neighborhood of the lamba point where they may be as large as 0.5 percent.

Approximately 125 calibration points have been taken on the same thermometer in such a way as to give a measure of the reproducibility. It was found that cycling between room temperature and liquid helium temperatures made no change in the resistance-temperature characteristic of the thermometer. Transferring the thermometer-heater assembly from one sample to another, which may have introduced slight mechanical strains, in some cases caused slight shifts in the T *vs* R curve. The total spread for the entire series of calibrations was less than 0.01°K over the whole range from 1° to 5°K.

The cusp in the calibration curves of Fig. 3 at about 2.2°K is, of course, not expected to be characteristic of the resistance-temperature relationship, but is thought to be due to an inaccurate relationship between temperature and the 1948 agreed temperature scale.

RESULTS

The heat capacity of a sample is obtained from a determination of the quantities on the right-hand side of Eq. (4). Heater current and potential drop and heating time are determined directly, as described in the experimental section. The mean temperature and the change in temperature during and due to heating, however, must be derived from resistance measurements of the thermometer. The resistance of the thermometer is, in general, known accurately enough to determine temperature to 0.0003°K. *Differences* in resistance, however, are known so that differences in temperature can be calculated to 0.0001°K.

From the combination of the data[1] for the silver holder and the silver sample, the heat capacity of the addenda and the atomic heat of silver have been determined. Since the measurements on the holder and the silver sample were not made at the same temperatures, it was necessary to smooth the holder data to combine with the data on the silver sample. The addenda cor-

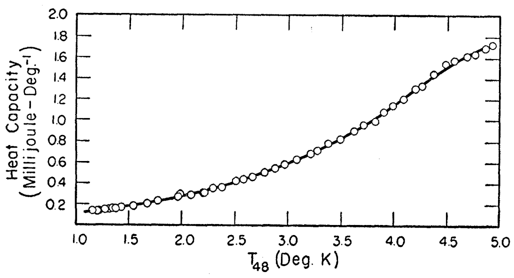

FIG. 4. Heat capacity of addenda.

rection has been plotted in Fig. 4, and it is from this curve that the addenda correction has been taken to obtain atomic heats for copper and gold from the measured heat capacities.

If c/T is written as a function of T^2, Eq. (1) yields a straight line with intercept γ, and slope β. The copper, silver, and gold data are plotted in this way in Figs. 5, 6, and 7, respectively. Only temperatures up to 4.2°K are included since it is not believed that the helium vapor pressure-temperature scale is sufficiently well known to make this plot meaningful above 4.2°K. On this scale, it is seen that a straight line is a good approximation to the data for all three of the metals. A determination of the constants of the lines by the method of least squares (for temperatures up to 4.2°K) gives the values listed in Table II for γ_{48} and Θ_{48}. The probable errors are determined from the scatter of the data from the straight line on the assumption that the errors are random. [In fact, the errors are not random but show a systematic deviation from Eq. (1) as shown in Fig. 8.]

In the experimental section an experiment to determine the effect of residual gas was described. The results of this experiment are plotted in Fig. 9. There are no observable differences between the measured heat capacities with gas and those without down to 1.4°K. Since the resolution corresponds to less than 1 percent of the heat capacity of the samples, it is concluded that there is no effect of gas down to 1.4°K.

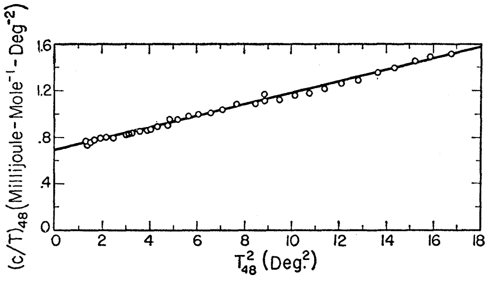

FIG. 5. Atomic heat of copper.

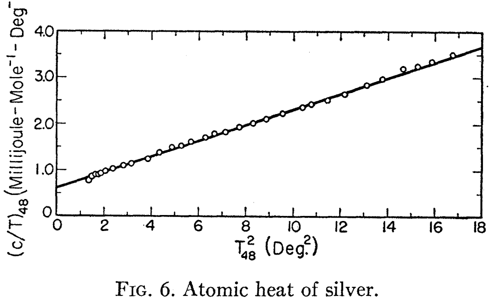

FIG. 6. Atomic heat of silver.

The sample of copper reported on previously[5] was different from the sample being reported here, having a different analysis and history. It is reassuring to find that the present sample yields essentially the same values for the constants, γ_{48} and Θ_{48}, to within the accuracy of the former experiment.[15] The silver and gold results are also in agreement with our previous results.[15]

Recently, improvements to the 1948 helium vapor pressure-temperature scale have been proposed which include the whole temperature region from 1.0° to 5.2°K. Erickson and Roberts[16] have found inaccuracies in the 1948 scale in the region from 1.0° to 4.2°K from their measurements on magnetic susceptibilities of paramagnetic salts. Berman and Swenson[17] have proposed a new relationship between helium vapor pressure and temperature from 4.2°K to 5.2°K from a comparison of the vapor pressure of helium with a gas thermometer. The results of our experiments also suggest that the 1948 temperature scale is inaccurate. Figure 8 shows that all three noble metals have systematic deviations from Eq. (1). Since all three, although they have different lattice and electron heat capacities, show the same fractional deviations, it is probable that the deviations are attributable to the temperature scale. For this reason we have set up a

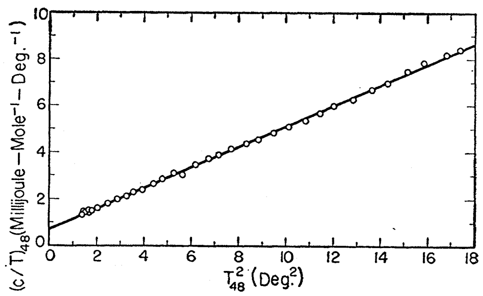

FIG. 7. Atomic heat of gold.

TABLE II. Atomic heat constants calculated from 1948 "agreed" temperature scale.

	Cu	Ag	Au
γ_{48} (millijoules-mole^{-1}-deg^{-2})	0.688±0.004	0.609±0.009	0.70±0.02
Θ_{48}(deg K)	343.2±1.3	225.0±0.5	164.1±0.3

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[15] Although the values reported at the conference were correct, the abstract for the conference gave values of γ_{48} that were a factor of 10^3 too large for all three metals. Also the comment about the temperature variation of Θ for the metals, which appears incorrectly in the abstract, was not given in the actual report.

[16] R. A. Erickson and L. D. Roberts, Phys. Rev. **93**, 957 (1954).

[17] R. Berman and C. A. Swenson, Phys. Rev. **95**, 311 (1954).

temperature scale, T_w, for each of the metals, designed so that Eq. (1) represents our results with the corrected values of atomic heat, c_w, and corrected constants γ_w and β_w. This condition leads to the following equation relating the uncorrected and corrected quantities:

$$T_{48}-T_w=\frac{1}{c_{48}}\left\{\frac{\gamma_{48}-\gamma_w}{2}(T_{48}'^2-T_{48}^2)+\frac{\beta_{48}-\beta_w}{4}(T_{48}'^4-T_{48}^4)+\int_{T_{48}}^{T_{48}'}[\delta c_{48}]_s dT\right\}, \quad (6)$$

where $\delta c_{48}=c_{48}-\gamma_{48}T_{48}-\beta_{48}T_{48}^3$, and $[\delta c_{48}]_s$ is the smoothed deviation curve, and T_{48}' is a constant of integration, selected so that the corrected scale, T_w, and the 1948 scale, T_{48}, agree at T_{48}'. The normal boiling point of helium was selected as T_{48}' since, Berman and Swenson[17] found no correction at that temperature. For a complete specification of the corrected temperature scale, T_w, it remained to evaluate the two constants γ_w and β_w in Eq. (6). Arbitrarily, the temperatures 1.6°K and 2.9°K were chosen as convenient and well separated temperatures for evaluating the constants. The corrections at these two points are approximately those of a smooth curve through the magnetic data of Erickson and Roberts,[16] namely at $T_{48}=1.600$°K, $T_{48}-T_w=+0.005$°K and at $T_{48}=2.900$°K, $T_{48}-T_w=+0.001$°K. The constants γ_w and β_w were then evaluated for each of the metals from Eq. (6). Temperature corrections, $T_{48}-T_w$, were calculated from Eq. (6) and plotted in Fig. 10. The points shown are from the magnetic data of Erickson and Roberts[16] below 4.2°K, and from the gas thermometry of Berman and Swenson[17] above 4.2°K. The agreement is within the scatter everywhere except below about 1.4°K where our data are suspect (A 1 percent to 2 percent error in the heat capacities would explain the low temperature disagreement.) The differences between the curves for copper, silver, and gold are within the experimental error. The curves of Fig. 10 are not meant to be a proposal of a new helium vapor pressure-temperature relationship, but are rather to be considered as confirming evidence of the temperature scale errors pointed out by Berman and Swenson[17] and by Erickson and Roberts.[16] Furthermore, these results are considered to demonstrate that the present measurements show that the atomic heats of the noble metals can be described by Eq. (1) to the accuracy with which the temperature scale is known.

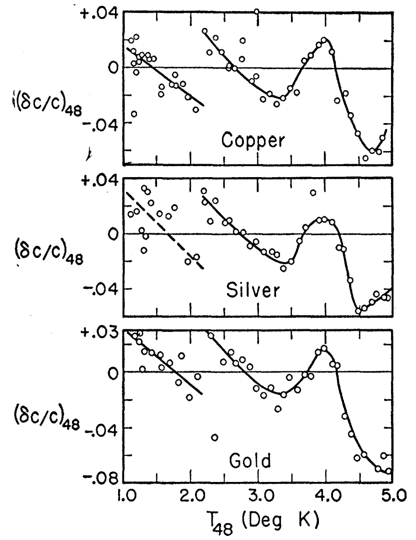

FIG. 8. Fractional deviation in atomic heats calculated on the 1948 temperature scale ($\delta c_{48}=c_{48}-\gamma_{48}T_{48}-\beta_{48}T_{48}^3$).

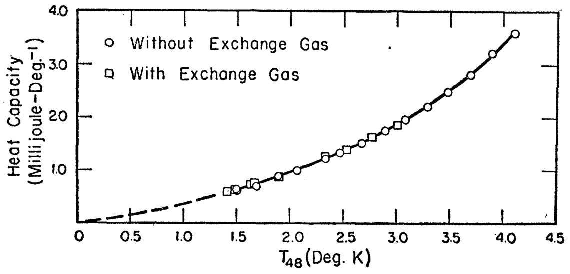

FIG. 9. Heat capacity of copper holder as determined with and without exchange gas.

Since it appears that any of the three curves of Fig. 10 gives temperatures, T_w, which are closer to the thermodynamic temperature than the temperatures from the 1948 "agreed" scale, the values of γ_w and Θ_w as calculated from Eq. (6) are given in Table III. These are believed to be better approximations than the values calculated on the 1948 scale. If the atomic heat is now calculated from these constants, and the difference between the calculated and measured values is plotted, it is seen that the errors are random (Fig. 11); indeed, the procedure employed here has forced randomization. The probable errors in γ_w and Θ_w calculated from this scatter is considerably smaller than those calculated for γ_{48} and Θ_{48}. (Two or three points for each

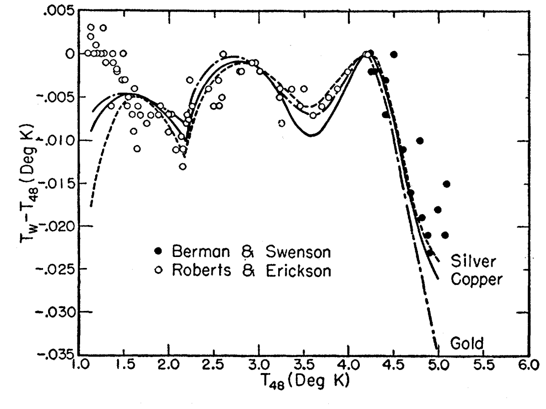

FIG. 10. Correction to the 1948 temperature scale calculated from the atomic heats of the noble metals.

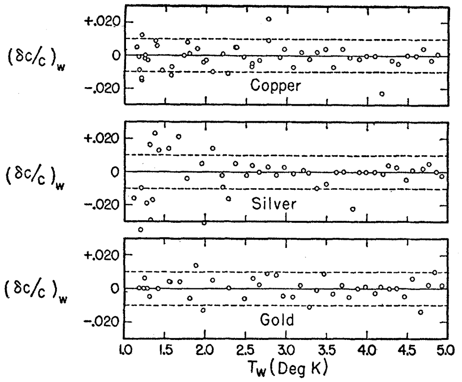

FIG. 11. Fractional deviations in the atomic heat calculated on the corrected temperature scale ($\delta c_w = c_w - \gamma_w T_w - \beta_w T_w^3$).

sample have been omitted from the plots of Fig. 11 since they were off the scale; however, they have been included in the estimate of the probable error.)

If the carbon resistance is recalibrated against one of the corrected temperature scales, then instead of the irregular curve of Fig. 3(c), the calibration becomes the smooth curve of Fig. 12. This is a much more reasonable dependence of resistance on temperature.

In order to estimate the probable error in a heat capacity determination at a temperature, T, errors in the following quantities are considered: (a) energy supplied to the sample; (b) the temperature rise of the sample; and (c) the mean value of the temperature.

The energy which is dissipated in the heater is determined from measurements of current, potential drop, and time of heating. These quantities all have uncertainties of less than 0.1 percent and therefore are not significant sources of error. However, it may be that not all of the energy dissipated in the resistance enters the sample and the addenda, but that a fraction may be drained off through the leads or may be carried off by the gas. The result of the experiment without gas shows that even at the lowest temperatures checked (about 1.4°K), the contribution of gas to the error in heat capacity of a sample is well under 1 percent and is negligible at higher temperatures. However, it is possible, since no experiment has been done to show otherwise, that an error of a few percent may occur from this source below 1.4°K. The heat that may be carried off through the leads has been estimated from the temperature rise of heater and thermometer, and appears to contribute less than 0.1 percent.

Errors introduced by uncertainty in the temperature rise due to heating are probably the largest sources of error of the experiment. The change in resistance is known accurately enough to determine temperature changes to about 0.6 percent. This results from limitations in reading and extrapolating the resistor potential drop *vs* time record and from limitations in the graphical interpolation of the temperature calibration curves. At the lowest temperatures, the drift rates are large, introducing a large uncertainty in extrapolation. This may contribute a percent or more error to the heat capacity measurements. There has been also introduced about a 0.1 percent rounding error from the calculations. These are all random errors and should show up in the results as scatter. The errors in heat capacity introduced by the uncertainty of the calibration of the thermometer, however, are systematic. They have been estimated to be less than 0.5 percent in the section on thermometry.

TABLE III. Atomic heat constants calculated from corrected temperature scale.

	Cu	Ag	Au
γ_w(millijoules-mole^{-1}-deg^{-2})	0.688±0.002	0.610±0.005	0.743±0.014
Θ_w(deg K)	343.8±0.5	225.3±0.2	164.57±0.14

Finally, the errors, resulting from the uncertainty in the thermometer current and potential drop measurements, in the mean temperature are less than 0.1 percent over the range of temperatures used. There are also uncertainties in temperature due to the inaccuracies of the calibration. These are systematic errors which are less than 0.1 percent except at the lowest temperatures.

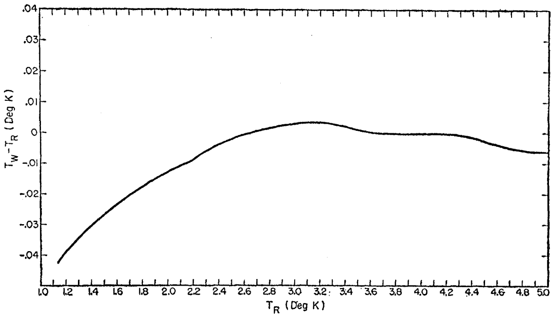

FIG. 12. Thermometer calibration curve using corrected temperature scale, T_w.

The errors which are expected to be statistical are about 0.8 percent to 0.9 percent. This is in agreement with the actual scatter (Fig. 11). The systematic errors that have been estimated above yield an uncertainty of 0.5 percent or less in a heat capacity determination.

There are still errors in heat capacity that are introduced by the uncertainty of the temperature scale. From the agreement between T_w and the temperature scale data of the authors quoted above,[16,17] these errors are expected to be everywhere less than 0.5 percent.

Table IV gives a comparison of our results with several calorimetric and indirect determinations of γ and Θ, for copper, silver, and gold. De Launay[18] and

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[18] J. De Launay, J. Chem. Phys. 22, 1676 (1954). Case 2 of this paper has been used for comparison with this work, since it is evident that as 0°K is approached the elastic constants determined by low-frequency velocity-of-sound measurements are appropriate and *not* the constants corrected by subtraction of the contribution of the conduction electrons.

TABLE IV. Comparison of atomic heat constants from this work with previous calorimetric and indirect determinations.

		Cu		Ag		Au	
		γ (millijoules-mole^{-1} deg^{-2})	Θ (°K)	γ (millijoules-mole^{-1} deg^{-2})	Θ (°K)	γ (millijoules-mole^{-1} deg^{-2})	Θ (°K)
Calorimetric	This work	0.688	343.8	0.610	225.3	0.743	164.57
	Keesom and Kok[a, b]	0.74	335	0.67	230	...	...
	Keesom and Pearlman[d]	...	...	0.645[c] 0.782[c]	229.0[c] 229.5[c]	...	...
	Esterman, Friedberg, and Goldman[e]	0.75	335	...	...	...	...
	Rayne[f]	0.72	...	0.67	...	...	...
Indirect	De Launay[g]	...	345.3	...	...	...	...
	Leighton[h]	...	345	...	229	...	...
	Schulz[i]	0.72	...	0.61	...	0.62	...
	Jones[j]	0.69	...	...	...	...	...

[a] See reference 3.
[b] See reference 4.
[c] The authors give two pairs of values for γ and Θ, one pair below ~2.0°K and one above.
[d] See reference 2.
[e] See reference 24.
[f] See reference 25.
[g] See reference 18.
[h] See reference 19.
[i] See reference 20.
[j] See reference 22.

Leighton[19] have calculated the values of Θ from the elastic constants. Schulz[20] reported values for the effective mass, m^*, of the electrons from the room temperature absorptivity of the metals. These have been converted to electronic heat capacities as in Wilson,[21] on the assumption that there is one conduction electron per atom. Jones'[22] value of γ for copper was obtained from a density-of-states calculation.

The agreement between the derived values of γ and our calorimetric determinations is as close as can be expected (with the possible exception of gold) on the basis of the accuracies of the various measurements and the approximations of the theory. This agreement with quantities, determined from high-temperature measurements, and the linearity of the electronic terms in the region 1°K to 5°K lend no support to a low-temperature variation of the electron density of states resulting from electron-lattice interactions.[7] Of course, these are metals which show a very weak electron-lattice interaction, as is known from the high-temperature resistance, and would thus give a relatively small effect.

The values of Θ derived from elastic constants are in excellent agreement with our calorimetric data. Except for copper, where the elastic constants have been recently measured,[23] small disagreements may be due to the errors in the elastic constants rather than to limitations of the model.

Finally, the comparison of our results with various other calorimetric data show that our values for γ, although often within the probable error of the other authors,[2–4,24,25] are generally low, for both silver and copper. Our Θ values, however, are in somewhat better agreement. In the case of silver, no evidence is found for an anomaly of the type reported by Keesom and Pearlman.[2]

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[19] R. B. Leighton, Revs. Modern Phys. **20**, 165 (1948). The elastic constants reported by De Launay (reference 18) are used here for copper in Leighton's equations to find Θ for copper.

[20] L. G. Schulz, Phys. Rev. **94**, 1422(A) (1954). The numerical values, which were given in the paper, do not appear in this abstract.

[21] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), pp. 44, 146.

[22] H. Jones, Proc. Phys. Soc. (London) **49**, 250 (1937).

[23] The measurements have been made by Overton, as reported in reference 18.

[24] Estermann, Friedberg, and Goldman, Phys. Rev. **87**, 582 (1952).

[25] J. Rayne, Phys. Rev. **95**, 1428 (1954).

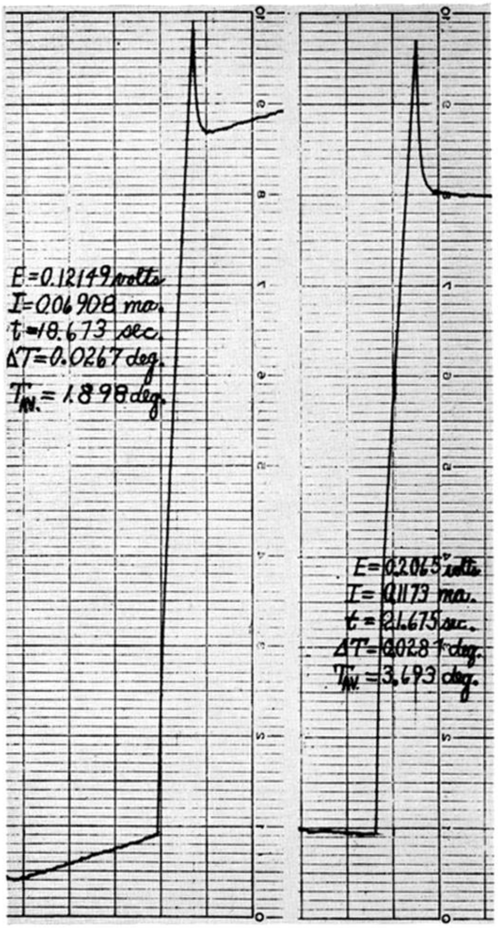

FIG. 2. Typical heating curves.