UNITED STATES DEPARTMENT OF COMMERCE
Alexander B. Trowbridge, *Secretary*
NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

# Critical Analysis of the Heat-Capacity Data of the Literature and Evaluation of Thermodynamic Properties of Copper, Silver, and Gold from 0 to 300 °K

George T. Furukawa, William G. Saba, and Martin L. Reilly

Institute for Basic Standards
National Bureau of Standards
Washington, D.C. 20234

NSRDS

## NSRDS—NBS 18

## National Standard Reference Data Series-
## National Bureau of Standards 18

(Category 5—Thermodynamic and Transport Properties)

Issued    April 1968

# Foreword

The National Standard Reference Data System is a government-wide effort to give to the technical community of the United States optimum access to the quantitative data of physical science, critically evaluated and compiled for convenience. This program was established in 1963 by The President's Office of Science and Technology, acting upon the recommendation of the Federal Council for Science and Technology. The National Bureau of Standards has been assigned responsibility for administering the effort. The general objective of the System is to coordinate and integrate existing data evaluation and compilation activities into a systematic, comprehensive program, supplementing and expanding technical coverage when necessary, establishing and maintaining standards for the output of the participating groups, and providing mechanisms for the dissemination of the output as required.

The NSRDS is conducted as a decentralized operation of nation-wide scope with central coordination by NBS. It comprises a complex of data centers and other activities, carried on in government agencies, academic institutions, and nongovernmental laboratories. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data.

For operational purposes, NSRDS compilation activities are organized into seven categories as listed below. The data publications of the NSRDS, which may consist of monographs, looseleaf sheets, computer tapes, or any other useful product, will be classified as belonging to one or another of these categories. An additional "General" category of NSRDS publications will include reports on detailed classification schemes, lists of compilations considered to be Standard Reference Data, status reports, and similar material. Thus, NSRDS publications will appear in the following eight categories:

| Category | Title |
|---|---|
| 1 | General |
| 2 | Nuclear Properties |
| 3 | Atomic and Molecular Properties |
| 4 | Solid State Properties |
| 5 | Thermodynamic and Transport Properties |
| 6 | Chemical Kinetics |
| 7 | Colloid and Surface Properties |
| 8 | Mechanical Properties of Materials |

The present compilation is in category 5 of the above list. It constitutes the 18th publication in the new NBS series known as the National Standard Reference Data Series.

A. V. Astin,
*Director.*

# Contents

# Critical Analysis of the Heat-Capacity Data of the Literature and Evaluation of Thermodynamic Properties of Copper, Silver, and Gold from 0 to 300 °K

## George T. Furukawa, William G. Saba, and Martin L. Reilly

The literature sources of heat-capacity data on copper, silver, and gold between 0 and 300 °K have been compiled and the data critically analyzed. Tables of heat capacity $(C_p)$, enthalpy $(H - H_0^\circ)$, entropy $(S^\circ)$, Gibbs energy $(G - H_0^\circ)$, enthalpy function $\left(\dfrac{H - H_0^\circ}{T}\right)$, and Gibbs energy function $\left(\dfrac{G - H_0^\circ}{T}\right)$ have been obtained from the analyses. The literature values of the heat capacity, the electronic coefficient of heat capacity $(\gamma)$, and the 0 °K limiting Debye characteristic temperature $(\theta_D(0))$ are compared with the selected values. The sources of the data are tabulated chronologically along with the temperature range of measurements, purity of sample, and the pertinent experimental procedures used. A bibliography of the references is listed. A brief appraisal of low-temperature calorimetry is given.

Key Words: Calorimetry, copper, Debye theta $(\theta)$, electronic coefficient of heat capacity, enthalpy, entropy, Gibbs energy, gold, heat capacity, silver, temperature scales, thermodynamic properties.

## 1. Introduction

This publication is the first of a series on the intensive examination of low-temperature heat-capacity data of the literature to be issued in connection with the mission of the National Standard Reference Data System. The objective of this series of publications is to present critically evaluated tables of heat capacity and the derived thermodynamic properties between 0 and 300 °K to meet the needs of physical chemists, physicists, and engineers. In the investigation of chemical equilibria and thermodynamic properties the interest is most often at the higher temperatures (room temperature and above). The effect of small uncertainties in the evaluation of the heat capacities at the lowest temperatures (below about 50 °K) is usually less significant to these quantities. Aside from precise cryogenic design applications, accurate heat-capacity data at the lowest temperatures are, however, indispensable in studies of lattice dynamics, energy states of magnetic materials, electronic distributions, order-disorder processes, and critical phenomena. Heat capacity is that property through which most experimental observations and theories of physical properties can be correlated and tested. Heat-capacity measurements can be experimentally realized with high accuracy. The data at the lowest temperatures have, therefore, been evaluated as carefully as the accuracy of the measurements would permit.

The scope of this series of publications is as follows:

1. From selected "best" values of heat capacity the derived thermodynamic properties (enthalpy, entropy, Gibbs energy, enthalpy function, and Gibbs energy function) will be calculated and given in tabular form. Although the upper limit of the tabular values will be 300 °K, selected data whenever available up to 400 or 450 °K will be included in the overall assessment. In the range 300 to 450 °K, the directly observed heat-capacity data will be used wherever possible. If only relative-enthalpy data are available, comparisons will be made in terms of the observed enthalpy increments at the lowest temperatures. This procedure will be followed because the 300 to 450 °K range is generally the lower extreme of the temperature range of relative-enthalpy measurements and the bulk of the existing equations representing the measurements have been fitted to minimize the absolute deviations over the complete range of relative-enthalpy observations. The one or possibly two relative-enthalpy observations between the reference temperature and 450 °K would, therefore, have comparatively little influence on the nature of the overall equation. Depending upon the type of material being investigated, states of thermodynamic equilibrium may also not prevail over the complete range of measurements. In most cases the values of heat capacity derived from relative enthalpy equations do not, therefore, join smoothly with the directly observed values of heat capacity from the lower temperatures. The best values of heat capacity above 300 °K that were selected but not reported in this publication will be referred to as "expected" values.

2. As a part of the bibliographic information, a comprehensive listing of low-temperature heat-capacity data with sources of pertinent high-temperature data that were used in the analysis will be given in tabular form in chronological order

1

of the journal publication date. Temperature range of measurements and, when available, the purity and physical state of the sample investigated will be given for each data source. The values of the 0 °K limiting Debye characteristic temperature, $\theta_D(0)$, the electronic coefficient of the heat capacity, $\gamma$, and the entropy at 298.15 °K will also be tabulated along with the precision or estimated uncertainty figures whenever they were published.

A number of publications exist with corrections or reinterpretation of data published earlier by the same authors. In some cases earlier "letters" are amplified or revised in subsequent publications. Whenever this occurred, the new values will be used in the analysis but the tabular chronological location of the first publication will be retained. Whenever reports, theses, and journal publications are available on the same set of measurements, the journal publication date will determine the chronological location in the bibliography of data sources. When more than one literature reference is given for a set of measurements, one of the above cases is indicated.

In the analysis of the heat-capacity data, the calorimetric procedures used in obtaining the data were examined. The details of calorimeter design, the method for cooling the sample, the thermometer for determining the temperature change, and the temperature scale are given along with the sources of experimental data.

3. In addition to providing the "best" values of heat capacity, this series of publications will present deviation plots to demonstrate the relationship between the selected values (base line) and those of the literature, and boundary lines to show the limit of accuracy (estimated) of the best values. The plots should also permit rapid comparison of any new data that might become available. When the same set of data appears more than once in the literature, reference will be made to the authors' most appropriate publication. In certain cases a large number of unpublished experimental observations have been received from the authors. These observations will be plotted whenever practical.

The plots include curves representing the $dC/dT$ of the selected values. The curves will show the smoothness of the selected values and general information on the manner in which the heat capacity changes with temperature. The plots will also show $\theta_D(T)$ calculated for the selected values using the relations:

$$C_v = C_p - \gamma T - \underline{A} C_v^2 T, \tag{1}$$

$$\underline{A} = v\beta^2/kC_v^2, \tag{2}$$

and

$$D(\theta/T) = C_v/3R, \tag{3}$$

where

$v = $ specific volume,
$\beta = $ coefficient of thermal expansion,
$k = $ coefficient of compressibility,
$D(\theta/T) = $ Debye function of $(\theta/T)$.

The value of $\underline{A}$ will be considered constant and the most appropriate value will be used. In this publication, $\underline{A}$ was obtained by an iterative method to fit the data best above 200 °K according to eq. (1). In addition to theoretical applications, the values of $\theta_D(T)$ are highly sensitive to the heat capacity, particularly at the higher temperatures, and are, therefore, useful in smoothing heat-capacity data of high precision.

4. The reported values of the 0 °K limiting Debye characteristic temperature, $\theta_D(0)$, and electronic coefficient of the heat capacity, $\gamma$, will be given on line plots, with the frequency of values reported shown by the number of literature references made to the locations on the line. The selected values of $\gamma$ and $\theta_D(0)$ will be given on the same plot along with their estimated uncertainties.

5. Search of the literature will be as current and complete as practical. Limited data or measurements incidental to measurements on other substances may, however, be overlooked because of lack of reference to the data or the title not being descriptive of the measurements.

6. The pertinent bibliography of the literature sources that have been examined, arranged alphabetically by author with the title of the publication and journal reference, will be at the end of each publication. A small number of references may be found late in the study. These will be appended, alphabetically arranged, to the first set.

## 2. Units, Symbols, Abbreviations, and Definitions

In this paper the following units, symbols, abbreviations, and definitions are used:

cm = centimeter
g = gram
sec = second
atm = atmosphere (pressure)
    1 atm = 101,325 N/m²
J = joule = $10^7$ ergs
mJ = millijoule = $10^{-3}$ J = $10^4$ ergs

cal = defined thermochemical calorie = 4.1840J
mol = mass of a pure substance corresponding to the formula weight in grams based on C-12 [20]
$t$ °C = temperature, $t$ degrees Celsius
$T$ °K = temperature, $T$ degrees Kelvin, triple-point of water = 273.16 °K
$\theta_D(0) = $ 0 °K limiting Debye characteristic temperature in °K, calculated from heat-capacity data.

2

$\theta_D(T) =$ Debye characteristic temperature at $T$ °K, calculated from experimental heat capacity at $T$ °K after subtracting nonlattice heat capacities and $(C_p - C_v)$.

$\gamma =$ electronic coefficient of heat capacity, in mJ °K$^{-2}$ mol$^{-1}$.

$C =$ heat capacity

$C_p =$ heat capacity at constant pressure (1 atm)

$C_v =$ heat capacity at constant volume

$H =$ enthalpy

$S =$ entropy

$G =$ Gibbs energy

$Q =$ quantity of heat

$W =$ watt $=$ J sec$^{-1}$

$R =$ gas constant $= 8.3143$ J °K$^{-1}$ mol$^{-1}$

$\underline{R} =$ resistance in ohms

$\underline{W} =$ resistance ratio $= \underline{R}_T/\underline{R}_0$ °C, the resistance at $T$ °K to that at 0 °C.

The prevailing energy unit of this publication will be the MKSA unit of energy, the joule. The tables of thermodynamic properties have been calculated on the basis of joules. For the convenience of a number of scientists who are more comfortable with calories, tables of thermodynamic properties in calories have been placed in the appendix.

The molal quantities have been converted to the basis of the 1961 atomic weights based on carbon 12 [20][1] whenever the experimental data warranted the conversion.

In tables 1, 3, and 5, certain abbrevations have been used to describe the experimental methods. The abbreviations used are defined as follows:

*Calorimeter Design*

VI–I = isothermal vacuum calorimeter operated by incremental heating.

VA–I = adiabatic vacuum calorimeter operated by incremental heating.

VA–C= adiabatic vacuum calorimeter operated by continuous heating.

GA–I = gas-filled adiabatic calorimeter operated by incremental heating.

GI–I = gas-filled isothermal calorimeter operated by incremental heating.

*Thermometer*

TC = thermocouple

PRT = platinum-resistance thermometer

Pb = Pb-resistance thermometer

Au-Ag = gold-silver alloy resistance thermometer

C = carbon-resistance thermometer

Ge = germanium-resistance thermometer

Cu = copper-resistance thermometer

MS = magnetic-susceptibility thermometer

*Temperature Scale*

ITS = International Temperature Scale (since 1960 International Practical Temperature Scale) [106].

vp = vapor pressure

gas = gas thermometer

TC = thermocouple scale initially compared with a gas thermometer.

MS = temperatures based on the magnetic susceptibility of paramagnetic salts.

year He = helium vapor pressure scale with official recognition.

vp-He = helium vapor pressure scale with no official recognition.

SR–$^3$He = $^3$He vapor pressure scale based on the earlier measurements of Sydoriak and Roberts [107].

1948 $^4$He = $^4$He vapor pressure scale [112, 98].

1948 ER $^4$He = $^4$He vapor pressure scale [38, 113].

1948 R $^4$He = $^4$He vapor pressure scale [94].

1948 W $^4$He = $^4$He vapor pressure scale [28].

1955 E $^4$He = $^4$He vapor pressure scale [22, 23].

1955 K $^4$He = $^4$He vapor pressure scale [66].

1955 L $^4$He = $^4$He vapor pressure scale [111].

1958 $^4$He = $^4$He vapor pressure scale [14].

*Cooling of Sample*

gas = gas heat exchange with heat sink

liquid = direct liquid refrigerant cooling by immersion.

cond = condensation of refrigerant in a small chamber of the calorimeter vessel and subsequent removal.

circ = refrigerant circulation.

MHS = mechanical heat switch

SHS = superconducting heat switch

AD–MC = adiabatic demagnetization of a paramagnetic salt mechanically attached to the sample through a metallic thermal conductor.

Other details regarding each source of data are given in the text dealing with each of the elements.

# 3. General Appraisal of Low-Temperature Heat-Capacity Measurements

For most of the temperature range below about 400 °K modern heat-capacity calorimeters and associated instrumentation have advanced to the state that, with reasonable care, a precision better than 0.1 percent and accuracy of 0.1 to 0.2 percent can be achieved [19, 27, 80, 88, 114]. Below about 50 °K the precision and, consequently, the accuracy begin to deteriorate with decreasing temperatures because of the diminution in heat capacity while relative errors in the determination of the energy increments introduced and the corresponding temperatures of the system steadily increase.

In very careful work using calorimeters designed for a limited temperature range and using relatively large samples, accuracies of about 1 percent have been realized down to 1 °K [86, 87]. Ahlers [3] has shown recently with measurements on several copper samples that by using the same thermometer, temperature scale, and cryostat, the intra-laboratory precision of 0.1 to 0.2 percent could be

---

[1] Figures in brackets indicate the literature references on page 41.

achieved between 1 and 20 °K. Osborne, Flotow, and Schreiner [86, 87] compared values of the heat capacity of copper at 1.2 and 4.2 °K obtained by 13 laboratories and showed the average deviation to be 0.8 percent at these temperatures.

In the measurements at the lowest temperatures the errors become amplified if the heat capacity of the substance under investigation decreases relatively more rapidly than the "addenda," which include the thermometer, thermocouples, heater, lead wires, thermal contact agent (e.g., cement, grease, etc.) and the sample vessel. A sample vessel by necessity is constructed of a metal of good thermal conductivity and has, therefore, a relatively high heat capacity. Other factors that contribute to the decline in relative accuracy at the lowest temperatures include the comparatively larger heat leak, deterioration in thermometry, uncertainties in the temperature scale, and loss in thermal contact between the sample and addenda.

With a single-piece sample, such as a short metal rod, the use of a sample vessel is often avoided for the measurements at the lowest temperatures by attaching the addenda directly onto the sample. Corrections to the measured heat capacity are made using the known masses and heat capacities of the addenda components. Significant uncertainties do arise, in particular when the mass of sample is small, from errors in the masses of the addenda and their heat capacities. For example, the heat capacity of the cement used could be dependent on the curing condition or the apportioning of the lead wires to the addenda could be incorrect. These sources of errors are obviously avoided by the sample vessel technique in which two separate series of measurements are made.

For measurements at the lowest temperatures, cooling by means of a mechanical or superconducting heat switch is preferred to $^4$He exchange gas, because of the $^4$He heat of desorption effects. The mechanical heat switch can, however, introduce relatively large amounts of energy into the system when the mechanical contact is broken and unduly raise the sample temperature.

In the region above 90 °K many of the published heat-capacity data are based on the International Practical Temperature Scale [106]. There are, however, many data between about 15 to 300 °K based on copper-constantan thermocouples calibrated against gas thermometers and vapor pressures of hydrogen, oxygen, and nitrogen [49, 50, 99]. There are published considerable data between 10 and 300 °K, based on Pb-resistance thermometers and resistance tables originally obtained by comparison with gas thermometers and vapor-pressure measurements [26, 97]. No direct comparison of these temperature scales is available.

In the United States, the NBS–1955 provisional scale [60, 46] has largely been used for the region 11 to 90 °K. The scale is based on the resistances of platinum thermometers calibrated against a helium-gas thermometer in 1939. In 1955 the whole

scale was translated downward by 0.01 °K. Temperature scales based similarly on platinum-resistance thermometers calibrated against gas thermometers have been established more recently at the Pennsylvania State University (PSU) [82], Physico-Technical and Radio-Technical Measurements Institute (PRMI) [13], and National Physical Laboratory (NPL) [6]. Intercomparison of the four scales showed that between 20 and 90 °K the deviations from the mean of the four scales do not exceed ± 0.01 °K [85].

Heat-capacity determinations using resistance thermometry are dependent on the $dR/dT$ or essentially the "size of the degree" of the temperature scale. Heat-capacity results, obtained using the NBS–1955 and the IPTS, exhibit reproducible anomalies as large as 0.2 percent that are attributable to deviations of these temperature scales from the thermodynamic scale [47]. Barber and Horsford [8] recently compared a set of platinum-resistance thermometers against a gas thermometer between 90 and 273 °K and showed wide variations in the IPTS from the thermodynamic scale. Differences of almost 0.04 °K were found.

The Working Group of the Advisory Committee on Thermometry to the International Committee of Weights and Measures has recently been considering a provisional reference table of resistance ratios, $\underline{W}_T = \underline{R}_T / \underline{R}_0 \, ^\circ\text{C}$, of platinum thermometers as a function of the temperature for the range 12 to 273 °K which is as closely related to the thermodynamic scale as the present knowledge permits [85, 7]. The table was derived in two parts. The range 12 to 95 °K is based largely on the four temperature scales established at NBS, PSU, PRMI, and NPL [60, 82, 13, 6]. The range 90 to 273 °K is based on the work at NPL [8]. The two ranges are made coincident at 90.249 °K within 0.001 °K in $T$, 0.02 percent in $dT/d\underline{W}$, and 0.067 percent in $d^2T/d\underline{W}^2$. The new temperature scale, referred to as Provisional Reference Table CCT64, or its slight modification is expected to be adopted internationally in the near future. The analysis in future publications will be made on the new scale when enough heat-capacity data have been obtained or converted to the new scale.

Carbon- and germanium-resistance thermometers have been used in most of the recent heat-capacity measurements below about 20 °K. For precise temperature measurements carbon thermometers require calibration with every application at the low temperatures. Germanium thermometers have been found to be stable enough with respect to time and to cycling between room temperature and liquid helium temperatures [73, 37, 10] that they do not require calibration as often as carbon thermometers. The disadvantage of a germanium thermometer is its complex resistance-temperature relation. Calibration at closely spaced temperatures over the complete range of application is, therefore, required to obtain a properly behaved $d\underline{R}/dT$ versus $T$ relation for the thermometer. The

4

values of $d\underline{R}/dT$ should change smoothly with the thermodynamic temperature and any unknown anomalies in $d\underline{R}/dT$ will be reflected as anomalies in the heat capacity.

Many of the existing heat-capacity data below about 5 °K are based on the helium vapor-pressure temperature scales which are in turn based on the helium gas and magnetic susceptibility temperature scales or indirectly to these scales through resistance thermometers. The 1948 $^4$He scale [112, 98], based on the vapor-pressure measurements of Kamerlingh Onnes and Weber [64] and Schmidt and Keesom [102, 103] and the calculations of Bleaney and Simon [12] with experimental verification by Bleaney and Hull [11], has been shown to deviate significantly from the thermodynamic temperature scale [9, 38]. The 1955L [109] and 1955E [22, 23] $^4$He vapor-pressure scales are independently obtained adjusted scales which differ from each other at most by 4 mdeg [14]. The present 1958 $^4$He scale [14] between 0.5 and 5.2 °K is the result of cooperative efforts of the groups that originated the 1955L and 1955E scales to decide upon a single scale. The estimated uncertainty from the absolute temperature scale given for the 1958 $^4$He scale is ±0.002 °K between 1 and 4.5 °K and larger uncertainties at temperatures above 4.5 °K [14].

The 1962 $^3$He vapor-pressure scale [102] is useful between 0.2 and 3.3 °K. The scale, based on the 1958 $^4$He scale [14] and thermodynamic properties of $^3$He between 0.2 and 2.0 °K, was developed by Roberts, Sherman, and Sydoriak [109, 107, 95]. Prior to the establishment of the above scale some of the measurements had been based on the earlier vapor-pressure measurements on $^3$He reported by Sydoriak and Roberts [107] in 1957.

The vapor pressure of hydrogen compiled by Woolley, Scott, and Brickwedde [116] and the more recent measurements of Hoge and Arnold [59] have been used for thermometer calibration in the range of about 14 to 20 °K. The vapor-pressure measurements of Hoge and Arnold [59] were based on the NBS–1939 scale [60].

Gas thermometers have been used for calibration in the region 5 to 15 °K to fill the gap left by the helium and hydrogen vapor-pressure scales [44, 87].

Germanium-resistance thermometers can now be calibrated at the National Bureau of Standards (U.S.) between 2 and 20 °K against germanium thermometer standards that have previously been calibrated against an acoustical thermometer [90]. The acoustical thermometer scale has been shown to be higher than the 1958 $^4$He scale by 0.006 °K at 2.323 °K, 0.007 °K at 2.807 °K, 0.008 °K at 3.211 °K, 0.010 °K at 4.212 °K, and 0.012 °K at 5.024 °K [90, 21]. Except at the lower temperature limit (11 °K) of the NBS–1955 scale, the acoustical thermometer and the NBS–1955 scales agree within ±0.005 °K [90]. Not enough heat-capacity data have been accumulated at this time to compare the results from different laboratories using this new temperature scale referred to as NBS Provisional Temperature Scale 2–20(1965).

## 4. Analysis of the Heat-Capacity Data on Copper, Silver, and Gold

In the past few years the intensive interest in the effect of alloying on the electronic heat capacity has resulted in a large number of publications on the heat capacity of copper, silver, and gold in the range below 4 °K on samples of 99.999 percent purity and higher. Unfortunately, in most of these publications the numerical values of the observed heat capacities have been omitted and, instead, the derived electronic coefficients of heat capacity $\gamma$ and 0 °K limiting Debye characteristic temperatures $\theta_D(0)$ have been reported. These values have been obtained from a plot of $C/T$ versus $T^2$ or by least-squares analysis of the experimental data to fit the equation:

$$C = \gamma T + AT^3 \tag{4}$$

or

$$C/T = \gamma + AT^2. \tag{5}$$

In some of the cases the equation was of the form:

$$C = \gamma T + AT^3 + BT^5 \tag{6}$$

or

$$C/T = \gamma + AT^2 + BT^4. \tag{7}$$

The coefficient $A$ yields the 0 °K limiting Debye characteristic temperature and corresponds to $12\pi^4 R/5[\theta_D(0)]^3$. The $B$ is the coefficient of the higher-order lattice term in $T^5$. The values of $\gamma$, $A$, and $B$ are expected to be slightly different depending upon the method used to obtain them. The precision figures that are reported with the values of $\gamma$ and $\theta_D(0)$ in many of these publications are not clearly defined. It is, therefore, difficult to decide whether such precision figures represent the precision of $\gamma$ and $\theta_D(0)$ or the observed heat capacities. The figures following the ± symbol found in the literature were given the interpretations defined in tables 1, 3, and 5 which list the sources of data analyzed.

Since the data analysis was to be performed in terms of heat capacities, each published set of values of $\gamma$ and $\theta_D(0)$ was first converted to heat capacities at regular temperature intervals between 0 and 5 °K. The final analysis was based on those calculated values of heat capacities corresponding to the experimental temperature range for which each set of $\gamma$ and $\theta_D(0)$ was obtained by the investigators.

A least-squares procedure was used with the high-speed digital computer to obtain the smoothed values of heat capacity between 0 and 300 °K from the experimental data. In certain temperature regions some personal judgment was also applied.

5

Deviation plots reflect the relation between the observed data and the final selection. Deviations from the selected values of the published experimental data are plotted as points and heat capacities calculated from $\gamma$ and $\theta_D(0)$ are indicated as continuous curves over the experimental temperature range. The thermodynamic functions were calculated from the smoothed values of heat capacity by numerical integration using four-point Lagrangian integration coefficients [110]. The thermodynamic relations used were:

$$H_T^\circ - H_0^\circ = \int^T C_p^\circ dT \qquad (8)$$

$$S_T^\circ = \int^T \frac{C_p^\circ}{T} dT \qquad (9)$$

$$G_T^\circ - H_0^\circ = -\int^T S^\circ dT = (H_T^\circ - H_0^\circ) - TS_T^\circ. \qquad (10)$$

The thermodynamic functions $(H_T^\circ - H_0^\circ)/T$ and $(G_T^\circ - H_0^\circ)/T$ were obtained from values of eq (8) and (10) by dividing by the corresponding temperature $T$. The literature measurements are in general reported for ill-defined experimental pressure conditions. The conversion from undefined but relatively low pressures to one atmosphere is considered negligible for solids. The values tabulated in this study are thus defined to be at 1-atm pressure.

In the following sections the data sources for each element are discussed and assessed. This is followed in succession by tabular chronological arrangement of the data sources, line plots of $\gamma$ and $\theta_D(0)$, plots of the deviations of the literature data from the selected best values of heat capacity, and the tables of thermodynamic properties. The line plots of $\gamma$ and $\theta_D(0)$ include the selected values of these quantities with their estimated uncertainties. The deviation plots give the limits of the estimated uncertainty of the selected values of heat capacity. The plots of $dC/dT$ and $\theta_D(T)$ as a function of the temperature are given for the selected values. The literature search is current to March 1967.

### 4.1. Copper (Cu, 63.54), Assessment of the Data Sources

Harper [56] reviewed the heat capacity and related data on copper published prior to 1914. For the present analysis no data on copper prior to 1914 were considered. Below about 100 °K very few of the data published before 1960 were given weight in the selection of the best values since they exhibited wide deviations from more recent measurements that are considered more precise. Most of the scatter can probably be attributed to inconsistencies in the temperature scales. Of the more recent data, the results of DuChatenier and DeNobel [34, 35] and Rorer, Onn, and Meyer [96] were not given any weight because of their excessive deviation (more than 3 percent) from all other data. Above 100 °K, more or less weight was given to the results reported by Harper [56], Eucken and Werth [41], Bronson, Chisholm, and Dockerty [15], Dockerty [32, 33] Maier and Anderson [74], Giauque and Meads [51], Sandenaw [100], and Martin [76].

The recent interest in the application of copper for a low-temperature heat-capacity reference [87] has resulted in the publication of several sets of smoothed values of heat capacity or heat-capacity equations based on experimental observations in the range 1 to 30 °K. These data are compared with the selected values in figure 2d. The smoothed values reported between 3 and 30 °K by Frank, Manchester, and Martin [43] are shown to deviate on the average about $\pm 0.3$ percent from the selected values. More recent measurements were reported between 3 and 30 °K by Martin [78]; below 15 °K, these values are on the average about 0.5 percent lower than his earlier measurements [43] and between 15 and 30 °K, the two sets of measurements differ from each other by about 0.2 percent. Ahlers [3] reported a six-term polynomial equation in odd powers of $T$ from 1 to 11 obtained by a least squares fit to 153 observations between 1.3 and 20 °K. The maximum deviation of the equation from the selected values is $-0.4$ percent. More recently, Osborne, Flotow, and Schreiner [87] reported a "reference equation" containing similar terms as those of Ahlers [3] based on new measurements and previously published data. The reference equation is within $\pm 0.1$ percent of the selected values. When a polynomial equation containing the same powers of $T$ was fitted by the method of least squares to the observations reported by Osborne, Flotow, and Schreiner [87], the equation obtained was found to deviate by $\pm 0.2$ percent from the selected values. The observations of Osborne, Flotow, and Schreiner [87] deviate on the average by $\pm 0.1$ percent from the equation obtained.

Harper [56] reported measurements from 0 to 50 °C (273 to 323 °K) on a 99.87 percent copper wire sample. The average deviation of the observations from a linear equation is reported to be 0.1 percent. His values are, however, slightly low and are on the average about 0.2 to 0.3 percent lower than the selected values.

A series of three papers on copper was published from the H. Kamerlingh Onnes laboratory. Keesom and Kamerlingh Onnes reported measurements in the range 15 to 22 °K [67] and 14 to 90 °K [68] on an electrolytic sample. The gold-resistance thermometer used was calibrated against the vapor pressure of hydrogen, a platinum-resistance thermometer, and a gas thermometer. The published results between 15 to 22 °K [67] scatter from $+6$ to $-2$ percent about the selected values, while those between 14 to 90 °K [68] scatter from $+2$ to $-5$ percent. The later observations of Kok and

Keesom [72] from 1.2 to 19.6 °K on a sample of 99.9 percent purity are on the average 5 percent higher than the selected values. Kok and Keesom [72] used phosphor-bronze and constantan-resistance thermometers calibrated against the vapor pressures of $^4$He and $H_2$ and a gas thermometer.

Eucken and Werth [41] reported measurements from 95 to 215 °K on electrolytic copper. A vacuum isothermal-jacket calorimeter was used. The temperatures were based on a Pb-resistance thermometer. Their values are, except for a few points, 0.2 to 0.4 percent higher than the selected values.

Mendelssohn and Closs [129] reported measurements from 5 to 15 °K. The measurements are presented graphically only with the average Debye characteristic temperature given as 315 °K. The low value is expected since the electronic contribution was not taken into account.

Bronson, Chisholm, and Dockerty [15] determined the heat capacity of several copper samples in the range −20 to 500 °C (253 to 773 °K) by the "method of mixtures" or the "drop method" and by the electrically heated adiabatic method. Only the results obtained with the adiabatic method in the range −5 to 110 °C (268 to 383 °K) have been considered in this analysis. The results reported by them are actually the copper equivalent of three copper calorimeters of about 1, 3, and 5 kg that were intended to be the "receivers" for the method of mixtures. Equations fitted to the three sets of measurements agreed within ±0.1 percent of each other. The 3- and 5-kg samples were considered to be "100 percent" pure and the 1-kg sample to be "especially" pure. All three sets of measurements are slightly lower than the selected values, being at most 0.2 percent lower.

Using an improved adiabatic calorimeter, Dockerty [32] determined the heat capacity in the range −72 to 116 °C (201 to 389 °K) of the 1-kg copper specimen used earlier by Bronson, Chisholm and Dockerty [15]. In the range of about 200 to 385 °K where the two measurements overlap, the values agree within 0.1 percent. The observations reported by Dockerty [32] are lower than the selected values, ranging from about 0.5 percent at 200 °K to 0.1 percent at 300 °K.

Dockerty [33] made further improvements by designing a vacuum adiabatic calorimeter and by reducing the mass of the adiabatic shield. (The earlier calorimeters used by Bronson, Chisholm, and Dockerty [15] and by Dockerty [32] were of the non-vacuum adiabatic type.) With the new calorimeter Dockerty [33] made measurements in the range 28 to 194 °K and test measurements around room temperature on commercially pure cold-rolled copper. The statement is made that his earlier measurements [32] with the nonvacuum type adiabatic calorimeter are too low by 0.2 percent and after corrections were made the agreement was within 0.05 percent of his new results obtained at 200 °K and room temperature. No information is given on how the corrections were made. Below

about 90 °K, Dockerty's new observations [33] scatter ±1 percent about the selected values but above 90 °K they are within ±0.1 percent.

Sykes [135] reported measurements from 369 to 834 °K (96 to 561 °C) using a continuous-heating method. Thermocouples were used for temperature measurements. The value at 369 °K is about 5 percent higher than the expected value. No weight was given to the data in selecting the final values.

Maier and Anderson [74] reported measurements from 53 to 294 °K on hard-drawn and annealed copper wire samples. The two series of measurements reported show no difference in heat capacity within 0.2 percent relative accuracy claimed. Their results, however, scatter as much as ±2 percent below about 100 °K but are within ±0.5 percent of the selected values above this temperature.

Honda and Tokunaga [125, 126] reported a single measurement at 298.6 °K (25.4 °C) on an electrolytic copper sample. A vacuum, isothermal-shield calorimeter was used. The temperature change was determined by means of a copper-constantan thermocouple. The reported value is about 1 percent lower than the selected value.

Thomas and Davies [136] reported measurements on a sample of 99.95 percent purity using a calorimeter in which the specimen was heated by eddy currents induced by an alternating magnetic field. Measurements were made at different frequencies ranging from 1775 to 1980 Hz. A thermocouple was used for the measurement of temperature change. The average of six observations at 293 °K (20 °C) is about 0.1 percent lower than the selected value.

Persoz [132] reported making measurements at five temperatures between 287 and 640 °K (14 and 367 °C) using a unique vacuum-adiabatic method. The sample was suspended within the sample vessel (copper shell) to achieve a relatively high degree of thermal isolation. The adiabatic shield was controlled relative to the sample vessel temperature. The sample when heated transferred heat to its vessel mainly by radiation. The temperatures of the sample and its vessel were observed as a function of time in the usual manner and the changes in temperature of the two parts were related to the respective heat capacities and to the electrical energy increment introduced to the sample. The two values at about 287 °K deviate + 0.2 and − 0.4 percent from the final selected values. The values reported at the higher temperatures deviate by larger amounts from the expected values.

Aoyama and Kanda [5] reported measurements from 82 to 273 °K on a sample of 99.92 percent purity, major impurities being Fe, C, and S at 0.02, 0.01, and 0.003 percent, respectively. The vacuum adiabatic method was used. Description of the method used for thermometry is not clear, but platinum-resistance thermometry was probably used. Their results are 1 to 2 percent higher than the selected values.

Giauque and Meads [51] reported measurements from 15 to 300 °K on an annealed sample of 99.96

percent purity. An isothermal-shield calorimeter was used. The temperatures were measured by means of a gold-silver alloy wire calibrated against a standard copper-constantan thermocouple [49, 50]. Below about 100 °K, the results reported by Giauque and Meads [51] deviate as much as $\pm 2$ percent from the selected values, but above 100 °K they are on the average about 0.4 percent higher.

Estermann, Friedberg, and Goldman [39] reported measurements from 1.8 to 4.2 °K on a polycrystalline sample of 99.6 percent purity. The principal impurity was Pb; the trace impurities found were Fe, Ni, and Ag. Helium exchange gas was used in cooling. The germanium-resistance thermometer used was calibrated on the vapor pressure of helium reported by Schmidt and Keesom [102, 103]. An error in the correction for the addenda in the results of Estermann et al. [39], was subsequently pointed out by Burk, Estermann, and Friedberg [18]. The value for $\theta_D(0)$ in the table has been adjusted for this correction. No correction was needed for $\gamma$. The relatively high value of $\gamma$ (0.75 mJ °K$^{-2}$ mol$^{-1}$) is consistent with the presence of Fe and Ni impurities and the relatively low value of $\theta_D(0)$ (340 °K) is also consistent with positive excess heat capacity observed by Franck, Manchester, and Martin [43] for Cu-Fe alloys containing small amounts of Fe. The heat capacities calculated from the corrected values of $\gamma$ and $\theta_D(0)$ reported by Estermann, Friedberg, and Goldman [39, 18] are on the average 6 percent higher than the selected values.

Rayne [133] reported measurements on a "commercial stock" copper sample of 99.9+ percent purity from 0.2 to 1 °K. In the experimental method, the copper sample was attached to a paramagnetic salt ($CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$) through a heavy-gage copper wire. The salt was used for adiabatic-demagnetization cooling of the copper sample and for the measurement of temperature. The 1948 $^4$He scale [112, 98] was compared with the magnetic susceptibility temperature scale based on the salt. Helium exchange gas was used in cooling the paramagnetic salt during the magnetization period. No numerical observations are given in the paper. The lattice contribution was considered negligible and the electronic coefficient of the heat capacity $\gamma$ based on the observations between 0.2 and 0.65 °K is given. The value of $\gamma$ reported (0.724 $\pm$ 0.033 mJ °K$^{-2}$ mol) is higher than most of the recently published values. The values of heat capacity based on the above value of $\gamma$ are significantly higher than the selected values (see figure 2c.1).

Hirano, Maniwa, and Takagi [124] reported measurements from about 323 to 723 °K (50 to 450 °C) on a sample of 99.998 percent purity using a vacuum-adiabatic continuous-heating method. Thermocouples were used for temperature measurements. The observations are presented graphically only on the sample slowly cooled from 873 °K (600 °C) and on the sample quenched from 873 °K to room temperature and annealed at 403 °K (130 °C). Sig-

nificantly higher values of heat capacity were observed between 423 and 623 °K (150 and 350 °C) when the sample was quench-annealed than when slowly cooled.

Corak, Garfunkel, Satterthwaite, and Wexler [28] reported measurements between 1 and 5 °K on an annealed sample of 99.999+ percent purity. Helium exchange gas was used for cooling. The carbon-resistance thermometer used was calibrated on the 1948 $^4$He scale [112, 98] and adjusted for deviation from the thermodynamic scale [38, 9]. Values of $\gamma$ and $\theta_D(0)$ reported are typical of those published and the calculated values of heat capacity are slightly lower than the selected values, the deviations ranging from about $-1$ percent at 1 °K to $-0.1$ percent at 5 °K.

Rayne [93] reported measurements from 1.5 to 4.2 °K on samples of 99.999 and 99.99 percent purity "as received" and a commercial alloy material containing 0.7 percent Cd and 0.5 percent Zn. Measurements were also made after annealing on the 99.99 percent sample. Cooling was achieved by means of a mechanical heat switch. A carbon-resistance thermometer used was calibrated on the 1948 $^4$He scale [112, 98] as adjusted by Erickson and Roberts [38]. The value of $\gamma$ is relatively low and that of $\theta_D(0)$ high for the 99.999 percent sample and calculated values of heat capacity are about 1 percent lower than the selected values. The values of $\gamma$ and $\theta_D(0)$ are relatively low for both of the measurements on the 99.99 percent sample. The $\theta_D(0)$ obtained for the 99 percent commercial alloy sample is in the range of most values published; the value 0.799 mJ °K$^{-2}$ mol$^{-1}$ obtained for $\gamma$ is exceptionally high.

In a subsequent paper Veal and Rayne [113] reported measurements from 1 to 4.2 °K on a sample of 99.999+ percent purity. A mechanical heat switch was used in cooling. No explicit statement on the temperature scale used is given. The 1955E $^4$He scale may have been used. The value of $\gamma$ and $\theta_D(0)$ are typical of those published and the calculated values of heat capacity range from $-0.3$ to $+0.5$ percent relative to the selected values.

Ramanathan and Srinivasan [91] reported measurements on an annealed sample of purity greater than 99.95 percent from 1.3 to 4.2 °K. A mechanical heat switch was used for cooling. The 1948 $^4$He scale [112, 98] was used. The value reported for $\gamma$ is relatively high and that of $\theta_D(0)$ relatively low. The calculated values of heat capacity range from 4.5 to 6.5 percent higher than the selected values. No weight was given to these data in the final series of analysis.

Griffel, Vest, and Smith [55] reported measurements from 1.8 to 4.2 °K on a 740 g sample of 99.99+ percent purity. A carbon-resistance thermometer calibrated on the 1955E $^4$He scale [22, 23] was used. Helium exchange gas was used for cooling. The values of $\gamma$ and $\theta_D(0)$ reported are typical of those published and values of heat capacity calculated

are in agreement with the selected values at 1.8 °K but deviate positively to almost 1 percent at 4.2 °K.

Sandenaw [100], using two calorimeters, reported measurements from 4 to 300 °K on "dead-soft" annealed, oxygen-free high-conductivity copper (OFHC). Analysis showed 99.96 percent purity. In one calorimeter, measurements were made from 4 to 300 °K and in the other from 36 to 300 °K. Except below about 60 °K, the results with the two calorimeters agree within about 1 percent. Above about 150 °K, the values reported by Sandenaw [100] are within about ±0.5 percent of the selected values. Below this temperature the deviation increases to as large as ±12 percent at around 10 °K.

Manchester [75] reported measurements from 1.2 to 4.2 °K on a sample of 99.999 percent purity. A mechanical heat switch was used for cooling. The carbon-resistance thermometer was calibrated on the 1955E $^4$He scale [22, 23]. The values of $\gamma$ and $\theta_D(0)$ are among the middle values of those published. Assumption is made that these measurements were reported again in the publication by Franck, Manchester, and Martin [43] to be discussed later.

Zimmerman and Hoare [118] reported measurements from 1.8 to 4.2 °K and from 3 to 16 °K on a single-crystal sample using two calorimeters, but no numerical data are given. The subsequent publication on measurements from 1.5 to 4.5 °K by Crane and Zimmerman [30] also do not give any numerical values.

Berge and Blanc [119] reported making measurements from 80 to 673 °K using the vacuum-adiabatic continuous-heating method. No information is given on the copper sample used in the measurements and no numerical values are reported. The temperatures were determined by means of thermocouples.

Martin [76] reported measurements from 20 to 300 °K on a commercially pure cold-rolled sample and on annealed and heavily cold-worked samples of 99.999 percent purity. The heavily cold-worked copper sample is shown to have on the average about 0.15 percent higher heat capacity than the annealed material. The results on the commercially pure cold-rolled material are between the above two samples. The measurements were made by means of an adiabatic calorimeter using a continuous-heating method. A copper resistance thermometer scale originally calibrated against a platinum-resistance thermometer was used. The results reported on the annealed sample by Martin [76] are within about ±0.2 percent of the selected values with predominance of the deviations being minus.

Franck, Manchester, and Martin [43] reported measurements from 0.4 to 30 °K on the same annealed sample of 99.999 percent purity used by Martin [76]. Three different calorimeters were used to cover the temperature range. A $^3$He cryostat was used in the range 0.4 to 1.5 °K. A superconducting Pb-wire thermal switch was used and temperatures were based on the $^3$He vapor-pressure measurements reported in 1957 by Sydoriak and Roberts

[107]. The calorimeter for the range 1.2 to 4.2 °K was the same as that used by Manchester [75]. A mechanical heat switch was used for cooling and temperatures were based on the 1955E $^4$He scale [22, 23]. The results reported for the 1.2 to 4.2 °K range in this later publication [43] are probably the same as those reported earlier by Manchester [75]. In the range 3 to 30 °K an adiabatic continuous-heating calorimeter was used. The cooling was achieved by condensing a small amount of helium in a small chamber attached to the sample holder and subsequently removing it by pumping. Temperatures were based on the 1958 $^4$He scale [14], vapor pressure of hydrogen [116], a gas thermometer [44], and the NBS-1955 provisional scale [60, 46]. The measurements obtained with the calorimeter for the range 0.4 to 1.5 °K yielded $\gamma = 0.682 \pm 0.011$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0) = 327 \pm 22$ °K and the values of heat capacity calculated using these values of $\gamma$ and $\theta_D(0)$ range from $-1.7$ percent at 0.4 °K to $+0.5$ at 1.5 °K from the selected values. The "smoothed" values reported are, however, within $-0.8$ percent of the selected values. Considering all of their results and those in the literature Franck, Manchester, and Martin [43] adopted the value 0.690 mJ °K$^{-2}$ mol$^{-1}$ for $\gamma$ and calculated $\theta_D(T)$ from the experimental data. The value $\theta_D(0) = 344$ °K was estimated from the values of $\theta_D(T)$. Their "smoothed" values between 0.4 and 1.5 °K are almost identical to the values calculated from $\gamma = 0.690$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0) = 344$ °K; their "smoothed" values were, therefore, probably derived from these "constants." The smoothed values reported between 1.2 and 4.2 °K are within ±1.2 percent of the selected values, while those calculated from $\gamma = 0.696$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0) = 344$ °K are within about $+0.2$ percent. The smoothed values reported for the calorimeter operated between 3 and 30 °K are on the whole about ±0.5 percent of the selected values, with somewhat better agreement over about one-half of the range.

Martin [127] reported measurements on annealed and cold-worked copper samples of 99.999 percent purity used earlier [76] after making modifications to the sample holder to permit the use of a conventional capsule-type platinum thermometer. The numerical values, reported only for the annealed sample between 16 and 90 °K, are on the average about ±0.4 percent of the final selected values. No numerical values are reported for the measurements made in the range 283 to 304 °K; the deviation plot for the annealed sample shows about ±0.1 percent deviation from the earlier measurements reported by Martin [76].

Martin [128] reported measurements in the range 0.5 to 1.5 °K on a vacuum-cast sample of 99.999 percent purity using a specially designed sample holder. The calorimeter was the same as that used in earlier measurements [43]. Thermal contact between the holder, in which the heater and thermometer were incorporated, and the sample was

achieved by multiple mechanical contacts maintained by means of springs and vacuum grease. A superconducting Pb-wire thermal switch was used in cooling the sample and the carbon thermometer was calibrated using the $^3$He vapor-pressure measurements reported in 1957 by Sydoriak and Roberts [107]. No numerical data were reported. A deviation plot given in the paper shows the measurements to be significantly higher than those reported earlier by Franck, Manchester, and Martin [43].

Du Chatenier and DeNobel [34, 35] reported measurements from 1 to 30 °K on a polycrystalline sample of 99.9999 percent purity. No impurities were detected by standard spectrographic methods. The temperatures were determined by means of a carbon resistor calibrated on the 1958 $^4$He scale [14] and on the vapor pressure of hydrogen reported by Hoge and Arnold [59]. Helium exchange gas was used for cooling. The relatively high value for $\gamma$ is consistent with possible heat of desorption at the lower temperatures but the relatively low value for $\theta_D(0)$ is inconsistent with this effect. These values are, however, consistent with the relatively high heat capacities reported by Du Chatenier and DeNobel. The heat capacities calculated between 1 and 5 °K using the values of $\gamma$ and $\theta_D(0)$ that were first reported [34] and the smoothed values of heat capacity between 1 and 30 °K [35] that were subsequently published are on the average about 4 to 5 percent higher than the selected values. The "sinusoidal" deviation of large amplitude from the selected values shown in figure 2b has also been found with silver and gold measurements reported from the same laboratory [35, 36].

O'Neal [84] reported measurements from 0.11 to 1.07 °K on a 900 g sample of 99.999 percent purity. Both a mechanical heat switch and a superconducting niobium-wire heat switch were used for cooling. A magnetic susceptibility temperature scale based on $2Ce(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ was used to calibrate a carbon film thermometer. The values of $\gamma$ and $\theta_D(0)$ reported are typical of those published and the calculated heat capacities are about 1 percent higher than the selected values.

Kneip, Betterton, and Scarbrough [71] made measurements from 1.2 to 4.5 °K on two very similarly vacuum-annealed samples of 99.999 percent purity from the same source. A mechanical heat switch was used in cooling and the carbon resistance thermometer was calibrated on the 1958 $^4$He scale [14]. The values of $\gamma$ are in close agreement with each other, but those of $\theta_D(0)$ differ by twice the estimated uncertainty given for each value. The heat capacities calculated from $\gamma = 0.697$ mJ °K$^2$ mol$^{-1}$ and $\theta_D(0) = 345.1$ °K are within about $\pm 0.2$ of the selected values, while those calculated from $\gamma = 0.696$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0) = 342.3$ °K deviate positively from 0.3 to 1.2 percent.

Phillips [89] reported measurements from 0.13 to 4.2 °K on a sample of 99.999 percent purity. Cooling was achieved by means of a combination of mechanical and superconducting niobium-wire switches.

Below 1 °K, the temperatures measured by me. of a carbon resistor were based on the magnetic susceptibility of $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$ and above 1 °K, on the 1958 $^4$He scale [14]. Values of $\gamma$ and $\theta_D(0)$ are typical of those published and the heat capacities calculated from them deviate positively from 0 to 0.5 percent from the selected values.

Ahlers [1, 2] made measurements from 2.3 to 19.7 °K on a sample of 99.999 percent purity. A germanium-resistance thermometer was used, calibration being made against the 1958 $^4$He scale [14] and the vapor pressure of hydrogen [116]. The values below 5 °K are about 1 percent higher than the selected values, while those above 5 °K are on the average 0.5 percent lower. Over 90 observations given in reference [1] have been plotted in figure 2b. Ahlers [1] attributes the relatively large deviations between 5 and 10 °K to errors in the temperature scale.

In a more recent publication Ahlers [3] reported measurements between 1.3 and 20 °K on four samples: a single crystal having the resistance ratio, $\underline{W} = \underline{R}_{300 \text{ °K}} / \underline{R}_{4.2 \text{ °K}}$, between 3000 and 6000 from one end to the other of the sample; annealed polycrystalline sample of 99.999 percent purity; severely cold-worked sample prepared from the annealed 99.999 percent material; and a chill-cast sample of 99.999 percent purity distributed by the Argonne National Laboratory in cooperation with the Calorimetry Conference (U.S.) [87]. The results on the annealed polycrystalline and chill-cast samples are essentially the same, i.e., within the $\pm 0.1$ percent precision of the measurements. The results on the single crystal are systematically slightly higher (0.2 percent) than those on the above two samples, actually outside by twice the limits of precision. The results on the cold-worked sample are decidedly higher, the difference being greater at the lower temperatures (about 0.7 percent below 6 °K). The higher values obtained for the cold-worked sample are consistent with the earlier work by Martin [76]. The heat capacities calculated from the published six-term equation based on the chill-cast sample follow very closely the selected values with small "oscillations" of maximum amplitude of $-0.4$ percent.

Isaacs and Massalski [63] and Isaacs [61] reported measurements from 1.6 to 4.2 °K using a carbon thermometer on a sample of 99.999 + percent purity. Sargent, Isaacs, and Massalski [101] reported later measurements using a germanium thermometer on annealed copper of 99.999 + percent purity from a different source. The values of $\gamma$ and $\theta_D(0)$ obtained are the same as those reported earlier [63, 61]. A mechanical heat switch was used for cooling and the temperatures were based on the 1958 $^4$He scale [14]. The values of $\gamma$ and $\theta_D(0)$ are typical of those published. Isaacs [62] recently recalculated the earlier published data [61, 63] after changing the formulation of the temperature-resistance relation of his thermometer and obtained $\gamma = 0.698 \pm 0.003$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0) = 342.2 \pm 0.8$ °K

which are not significantly different from the earlier values. The heat capacities calculated from them deviate positively between 0.6 and 1.2 percent from the selected values.

Dixon, Hoare, Holden, and Moody [31] reported measurements from 1.2 to 4.2 °K on chill-cast and annealed samples of 99.999 percent purity. The carbon-resistance thermometer used was calibrated on the 1958 $^4$He scale [14]. Cooling was achieved using a mechanical heat switch. The values of $\gamma$ and $\theta_D(0)$ obtained in the two measurements are essentially the same and are in agreement with other published values and the calculated heat capacities deviate positively on the average by 0.5 percent from the selected values.

Pawel and Stansbury [131] reported measurements from 363 to 883 °K (90 to 610 °C) on an electrolytic copper sample of 99.99 percent purity using a vacuum-adiabatic calorimeter. Platinum versus platinum-rhodium thermocouples were used in the temperature measurements. After correcting for variations that are dependent upon the heating rate, a precision of ±0.25 percent is claimed. Except for the observation at the lowest temperature (363 °K), where their reported value of heat capacity is about 0.2 percent lower than the expected values, the data at the higher temperatures tend to deviate positively. Very little weight was given to the data in selecting the best values in the region of 300 °K.

Senozan [134] reported making measurements on a sample of 99.999 percent purity from 0.25 to 25 °K. No numerical observations are reported. The values of $\gamma$ and $\theta_D(0)$ based on the measurements from 0.25 to 2 °K yield values of heat capacity that are from 0.4 to 0.8 percent higher than the final selected values. In cooling the sample, the thermal contact down to 78 °K was made using hydrogen exchange gas and below this temperature using mechanical heat switches. Germanium thermometers were used. Below 1.1 °K the temperatures were based on the magnetic susceptibility of $2Ce(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ (CMN), between 1 and 4 °K on the 1958 $^4$He scale [14], between 10 and 25 °K on a platinum-resistance thermometer (temperature scale not given), and between 4 and 10 °K on a carbon thermometer and an interpolation equation.

Rorer, Onn, and Meyer [96] made measurements from 0.4 to 4.0 °K on a sample of 99.99 percent purity. Cooling of the sample was done by a mechanical heat switch. The carbon-resistance thermometers used were calibrated on the 1958 $^4$He scale [14], 1962 $^3$He scale [104], and the magnetic susceptibility temperatures of $Cr_2(SO_4)_3 \cdot (CH_3NH_3)_2SO_4 \cdot 24H_2O$ and $2Ce(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$. The value of $\gamma$ obtained is relatively high and that of $\theta_D(0)$ is the lowest among a cluster of recently published values and the calculated heat capacities are on the average 3 percent higher than the selected values.

Martin [78] reported new measurements from 3 to 30 °K on the same annealed copper sample of 99.999 percent purity used earlier by Franck, Manchester, and Martin [43]. Improvements on his

earlier calorimeter are reported. A germanium-resistance thermometer was used and the temperatures were based on the 1958 $^4$He scale [14], vapor pressure of hydorgen [116], a gas thermometer [44], and the NBS–1955 provisional scale [60, 46]. The value of $\gamma = 0.696 \pm 0.005$ mJ °K$^{-2}$ mol$^{-1}$ reported earlier by Manchester [75, 43] was used to calculate $\theta_D(T)$ from the experimental data. The reported value of $\theta_D(0) = 345.6 \pm 1.0$ °K estimated from the values of $\theta_D(T)$, is the highest of those published. Below 10 °K the smoothed values reported deviate on the average by −0.4 percent from the selected values and above 10 °K within ±0.2 percent.

Clune and Green [24] reported two series of measurements from 2 to 4 °K on a sample of 99.999 percent purity. The carbon-resistance thermometer used was calibrated on the 1958 $^4$He scale [14]. A unique "adiabatic" technique was used in the measurements. The calorimetric method involved, at each selected temperature ($T_{eq}$), the adjustment of an auxiliary heater to compensate for the heat leak of the sample through a small thermal link to a heat sink maintained at 1.5 °K. The energy to heat the sample from $T_{eq} - \Delta T$ to $T_{eq} + \Delta T$ was then determined, the $\Delta T$ being symmetrically displaced about $T_{eq}$. The method allowed a number of measurements to be quickly repeated for each $T_{eq}$. Cooling was achieved by a mechanical heat switch. The method requires for maximum accuracy the unbalances in the heat leak below and above $T_{eq}$ to be compensated and the heating time to be shorter than the heat leak time constant but longer than the thermal equilibrium time constant of the sample and thermometer. Results of the two series of measurements show that their precision is better than the agreement in the values of $\gamma$ and $\theta_D(0)$ obtained. They are, however, typical of the values published. The heat capacities from one set of values of $\gamma$ and $\theta_D(0)$ deviate positively by not more than 0.3 percent from the selected values and those from the other set deviate positively from 0.7 to 0.3 percent in the range 2 to 4 °K.

Osborne, Flotow, and Schreiner [86, 87] reported measurements from 1 to 25 °K on an annealed sample of 99.999 percent purity prepared by the Argonne National Laboratory for distribution in cooperation with the Calorimetry Conference. The germanium-resistance thermometer used was calibrated on the 1958 $^4$He [14] and 1962 $^3$He [104] scales, vapor pressure of hydrogen, and a gas thermometer. A mechanical heat switch was used in cooling. The values of $\gamma$ and $\theta_D(0)$ reported are typical of those published. Below 2 °K the observed values reported are lower, as much as 0.5 percent, than the selected values and above 2 °K they are within ±0.3 percent. Osborne, Flotow, and Schreiner [87] obtained a six-term polynomial equation in odd powers of $T$ from 1 to 11 based on published data and their new measurements and applicable from 1 to 25 °K. The values of heat capacity from the equation are within ±0.1 percent of the selected values.

11

TABLE 1. *Sources of heat-capacity data on copper used in the analysis*

| Year | Temperature range of heat measurements °K | Purity of specimen Weight % | Electronic coefficient, γ mJ °K⁻² mol⁻¹ × 10³ | Debye θ at 0 °K °K | Entropy at 298.15 °K J °K⁻¹ mol⁻¹ | cal °K⁻¹ mol⁻¹ | Calorimeter design | Thermometer | Temperature scale | Cooling of sample | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1914 | 273–323 | 99.87 electrolytic | | | | | VI–I [e] | Cu [e] | PRT [e] | gas [e] | [56] |
| 1914 | 15–22 | electrolytic | | | | | VI–I | Au | vp-H₂, PRT, gas | gas | [67] |
| 1915 | 14–90 | electrolytic | | | | | VI–I | Au | vp-H₂, PRT, gas | gas | [68] |
| 1930 | 95–215 | electrolytic | | | | | VI–I | Pb | Pb, PRT, gas | gas | [41] |
| 1932 | 5–15 | ? | | 315 | | | VI–I | gas | gas | gas | [129] |
| 1933 | 253–773 | "100" | | | | | GA–I | PRT | ITS | gas | [15] |
| 1933 | 201–389 | 99.5 (cold-rolled) | | | | | GA–I | PRT | ITS | gas | [32] |
| 1934 | 54–294 | hard drawn wire | | | | | VI–I | Cu | TC, vp-H₂, vp-O₂, gas | gas | [74] |
| 1934 | 53–293 | annealed wire | | | | | VI–I | Cu | TC, vp-H₂, vp-O₂, gas | gas | [74] |
| 1935 | 298.6 | electrolytic | (Measurement was made at one temperature, 25.4 °C) | | | | VI–I | TC | ? | gas | [125, 126] |
| 1936 | 1.2–19.6 | 99.9 | 743 | 335 | | | VI–I | phosphor-bronze, constantan | vp-⁴He, vp-H₂, gas | gas | [72] |
| 1937 | 28–194 | commercially pure (cold-rolled) | | | | | VA–I | TC, PRT | ITS | gas | [33] |
| 1937 | 293 | 99.95 | (Measurement was made at one temperature, 20 °C) | | | | GI–I | TC | ? | gas | [136] |
| 1940 | 287–640 | ? | (Measurements were made at five temperatures) | | | | VA–I | PRT | ? | gas | [132] |
| 1941 | 82–273 | 99.92 | | | | | VA–I | PRT | gas | gas | [5] |
| 1941 | 15–300 | 99.96 (annealed) | | | 33.31 | 7.961 | VI–I | Au-Ag | TC, vp-H₂, vp-O₂, gas | gas | [51] |
| 1952 | 1.8–4.2 | 99.6 (polycrystalline) | 750 | 340 | | | VI–I | Ge | vp-⁴He | gas | [39, 18] |
| 1954 | 0.2–1 | commercial 99.9+ | 724 ±33 [a] | | | | VI–I | MS | MS, 1948 ⁴He | gas, AD-MC | [133] |
| 1955 | 1–5 | 99.999+ (annealed) | 688 ±2 [a] | 343.8 ±0.5 [a] | | | VI–I | C | 1948W ⁴He | gas | [28] |
| 1956 | 1.5–4.2 | 99.999 (as received) | 686 ±5 [b] | 345.1 ±3 [b] | | | VI–I | C | 1948ER ⁴He | MHS | [93, 113] |
| 1956 | 1.5–4.2 | 99.9 (as received) | 670 ±5 [b] | 338.9 ±3 [b] | | | VI–I | C | 1948ER ⁴He | MHS | [93, 113] |
| 1956 | 1.5–4.2 | 99.9 (annealed) | 670 ±5 [b] | 338.9 ±3 [b] | | | VI–I | C | 1948ER ⁴He | MHS | [93, 113] |
| 1956 | 1.5–4.2 | 99 (Cd 0.7%, Zn 0.5%) | 799 ±5 [b, c] | 344.7 ±3 [b] | | | VI–I | C | 1948ER ⁴He | MHS | [93, 113] |
| 1957 | 1.3–4.2 | 99.95+ (annealed) | 723 ±28 [a] | 334.0 ±1.6 [a] | | | VI–I | C | 1948 ⁴He | MHS | [91] |
| 1957 | 1.8–4.2 | 99.99+ | 691 ±6 [a] | 342 ±2 [a] | | | VI–I | C | 1955E ⁴He | gas | [55] |
| 1959 | 4–300 | 99.96 (OFHC) | | | 33.25 | 7.946 | VA–C | TC | TC, vp-⁴He vp-H₂, vp-N₂ | liquid | [100] |
| 1959 | 39–300 | 99.96 (OFHC) | | | 33.45 | 7.995 | VA–C | TC | TC, vp-⁴He vp-H₂, vp-N₂ | gas | [100] |
| 1959 | 1.2–4.2 | 99.999 | 696 ±5 [a] | 344 ±2 [a] | | | VI–I | C | 1955E ⁴He | MHS | [75, 43] |
| 1960 | 1.8–4.2 | single crystal | (No numerical data are given in the paper) | | | | VI–I | C | vp-⁴He | gas | [118] |
| 1960 | 3–16 | single crystal | (No numerical data are given in the paper) | | | | VI–I | C | gas | gas | [110] |
| 1960 | 80–673 | ? | (No numerical data are given in the paper) | | | | VA–C | TC | ? | gas | [119] |
| 1960 | 21–300 | commercially pure (cold-rolled) | | | | | VA–C | Cu | ITS | gas | [76] |
| 1960 | 20–300 | 99.999 (annealed) | | | 33.15 | 7.92 ±0.04 [b] | VA–C | Cu | ITS | gas | [76] |
| 1960 | 21–300 | 99.999 (cold-worked) | | | | | VA–C | Cu | ITS | gas | [76] |
| 1961 | 1.5–4.5 | "pure" | (No numerical data are given in the paper) | | | | VI–I | C | vp-⁴He | MHS | [30] |
| 1961 | 0.4–1.5 | 99.999 | 682 ±11 [a] | 327 ±22 [a] | | | VI–I | C | SR-³He | SHS | [43] |
| 1961 | 1.2–4.2 | 99.999 | | | | | VI–I | C | 1955E ⁴He | MHS | [43] |
| 1961 | 3–30 | 99.999 | | | | | VA–C | C | 1958 ⁴He, vp-H₂, gas, NBS-1955 | cond | [43] |

TABLE 1. *Sources of heat-capacity data on copper used in the analysis* — Continued

| Year | Temperature range of heat measurements °K | Purity of specimen Weight % | Electronic coefficient, γ mJ °K⁻² mol⁻¹ × 10³ | Debye θ at 0 °K °K | Entropy at 298.15 °K J °K⁻¹ mol⁻¹ | Entropy at 298.15 °K cal °K⁻¹ mol⁻¹ | Experimental method Calorimeter design | Experimental method Thermometer | Experimental method Temperature scale | Experimental method Cooling of sample | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1961 | 0.4–30 | 99.999 | 690 | 344 | | | | | | | [43] |
| 1962 | 16–90 283–304 | 99.999 (annealed) | | | | | VA–C [c] | PRT [c] | NBS–1955 [c] IPTS | gas [c] | [127] |
| 1962 | 16–90 283–304 | 99.999 (cold-worked) | (No numerical data are given in the paper) | | | | VA–C | PRT | NBS–1955 IPTS | gas | [127] |
| 1962 | 1–30 | 99.9999 | 721 | 338.9 | | | VI–I | C | 1958 ⁴He, vp-H₂ | gas | [34, 35] |
| 1962 | 1–4.2 | 99.999 | 692 ±7 [b] | 342.7 ±3 [b] | | | VI–I | C | vp-⁴He | MHS | [113] |
| 1963 | 0.11–1.07 | 99.999 (annealed) | 702 | 342.9 | | | VI–I | C | MS | MHS, SHS | [84] |
| 1963 | 1.2–4.5 | 99.999 (I) (annealed) | 697 ±7 [b] | 345.1 ±1.4 [b] | | | VI–I | C | 1958 ⁴He | MHS | [71] |
| 1963 | 1.2–4.5 | 99.999 (II) (annealed) | 696 ±7 [b] | 342.3 ±1.4 [b] | | | VI–I | C | 1958 ⁴He | MHS | [71] |
| 1964 | 0.5–1.5 | 99.999 | (No numerical data are given in the paper) | | | | VI–I | C | SR-³He | SHS | [128] |
| 1964 | 0.13–4.2 | 99.999 | 695 | 343.4 | | | VI–I | C | MS, 1958 ⁴He | MHS, SHS | [89] |
| 1964 | 2.3–19.7 | 99.999 | 704 | 344 | | | VI–I | Ge | 1958 ⁴He, vp-H₂ | MHS | [1, 2] |
| 1965 | 1.6–4.2 | 99.999+ | 698 ±2 [a] | 342.3 ±3 [b, d] | | | VI–I | C | 1958 ⁴He | MHS | [63, 61, 62] |
| 1965 | 1.2–4.2 | 99.999 (chill cast) | 695 ±1 [a] | 343.2 ±0.2 [a] | | | VI–I | C | 1958 ⁴He | MHS | [31] |
| 1965 | 1.2–4.2 | 999.999 (annealed) | 698 ±2 [a] | 343.2 ±0.4 [a] | | | VI–I | C | 1958 ⁴He | MHS | [31] |
| 1965 | 0.25–25 | 99.999 | 698 | 342 | | | VI–I | Ge | MS, 1958 ⁴He, PRT (?) | gas, MHS | [134] |
| 1965 | 0.4–4.0 | 99.99 | 720 ±8 [a] | 342 ±2 [a] | | | VI–I | C | 1958 ⁴He, 1962 ³He, MS | MHS | [96] |
| 1966 | 3–30 | 99.999 (annealed) | 696 ±5 [a] | 345.6 ±1.0 [a] | | | VA–C | Ge | 1958 ⁴He, vp-H₂, gas, NBS–1955 | circ | [78] |
| 1966 | 2–4 | 99.999 (annealed) | 702 ±2 [a] | 344.9 ±0.4 [a] | | | VA–I | C | 1958 ⁴He | MHS | [24] |
| 1966 | 2–4 | 99.999 (annealed) | 696 ±2 [a] | 344.1 ±0.4 [a] | | | VA–I | C | 1958 ⁴He | MHS | [24] |
| 1966 | 1.3–20 | 99.999 (chill cast) | 695 | 343.9 | | | VI–I | Ge | 1958 ⁴He, vp-H₂, gas, NBS–1955 | MHS | [3] |
| 1966 | 1–25 | 99.999 (annealed) | 694 | 344.5 | | | VI–I | Ge | 1962 ³He, 1958 ⁴He, vp-H₂, gas | MHS | [86, 87] |
| 1966 | 1.6–4.2 | 99.999+ (annealed | 698 ±2 [a] | 342.3 ±3 [b, d] | | | VI–I | Ge | 1958 ⁴He | MHS | [101] |

[a] These figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the precision of the values given.
[b] These figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the estimated uncertainties in the values given.
[c] Not included in the analysis or plotted in figure 1.
[d] Isaacs [62] recalculated the experimental observations and found $\gamma = 0.698 \pm 0.003$ mJ °K⁻² mol⁻¹ and $\theta_D(0) = 342.2 \pm 0.8$ °K.
[e] See section 2 for definitions of symbols and abbreviations used.

13
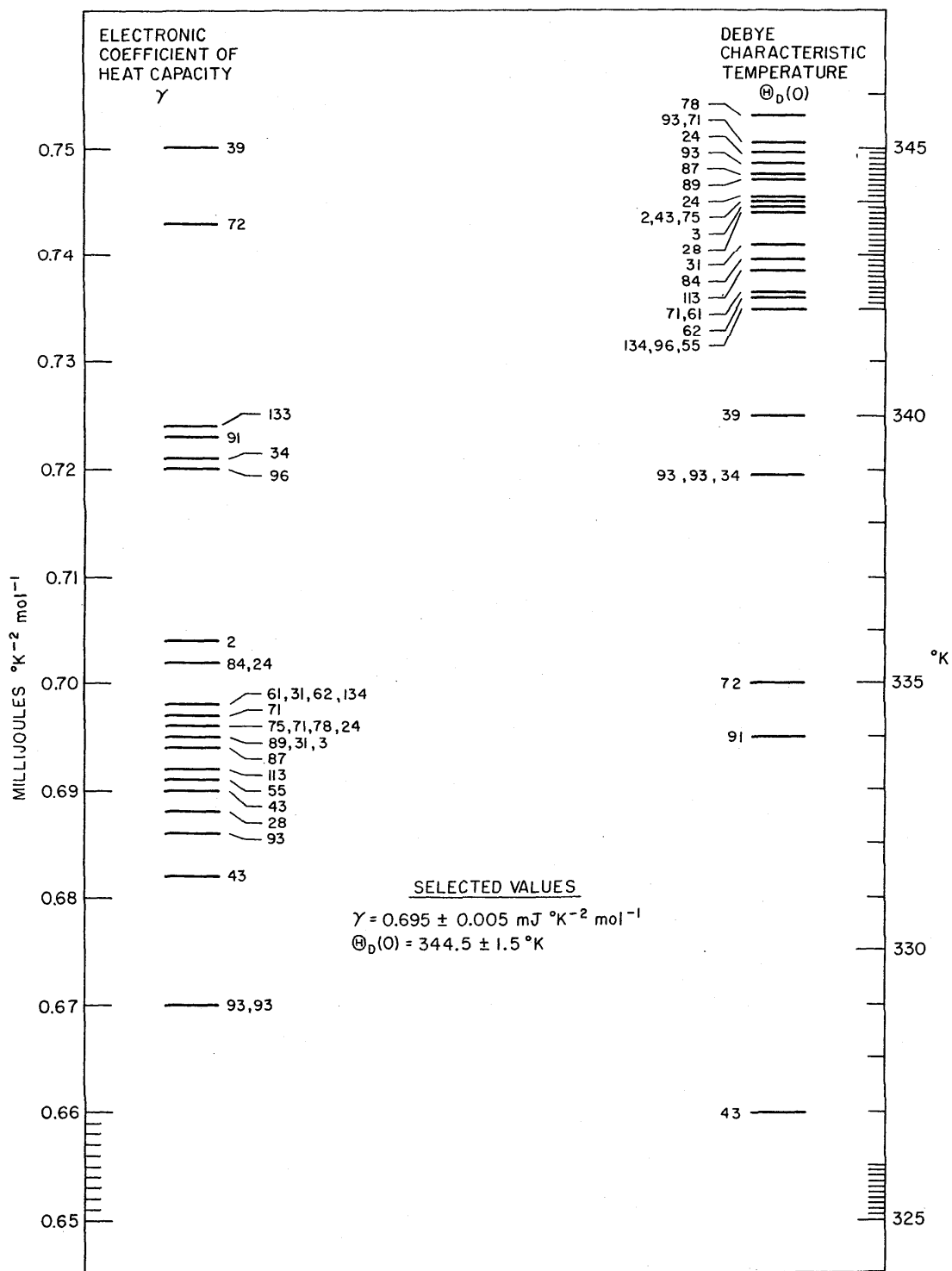
FIGURE 1. *Comparison of the reported values of electronic coefficients of heat capacity, γ, and Debye characteristic temperatures, $\theta_D(0)$. of copper.*

14
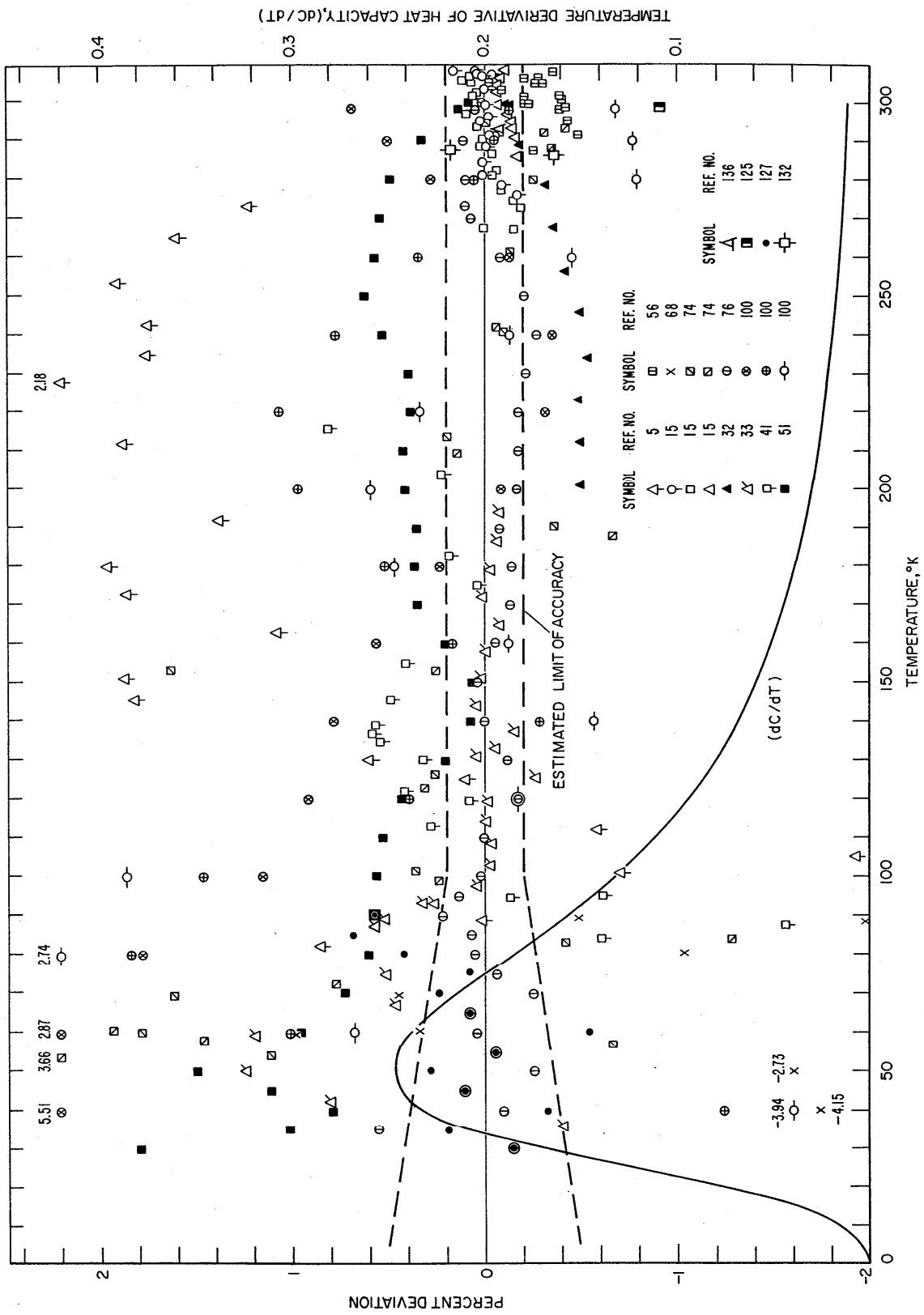
FIGURE 2a. *Deviations of the heat-capacity data of the literature on copper from the selected values in the range 30 to 300 °K.*
*The estimated limit of accuracy and the temperature derivative, dC/dT, in J °K⁻² mol⁻¹ of the selected values.*

15
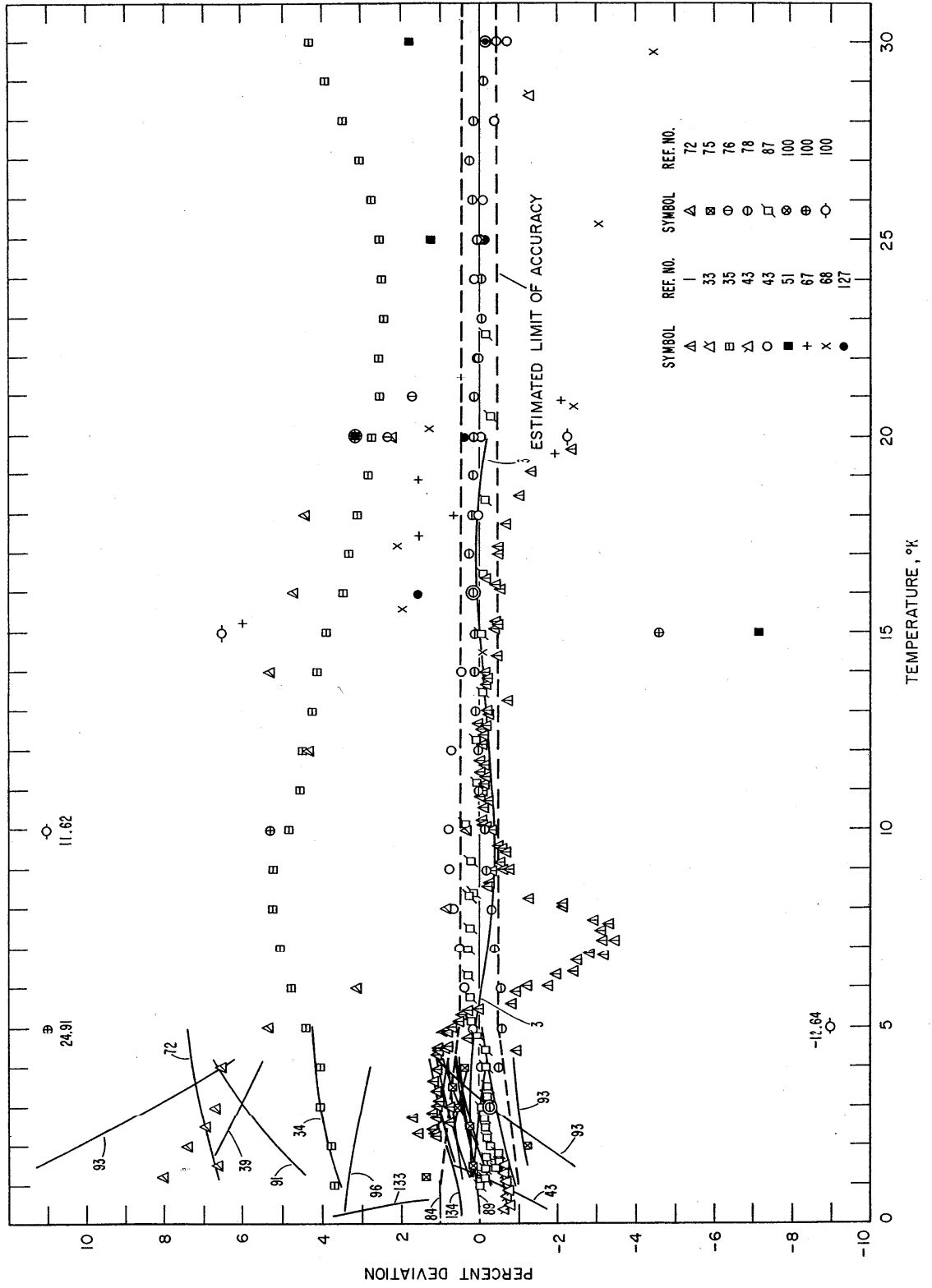
FIGURE 2b. *Deviations of the heat-capacity data of the literature on copper from the selected values in the range 0 to 30 °K and the estimated limit of accuracy of the selected values.*

16

91
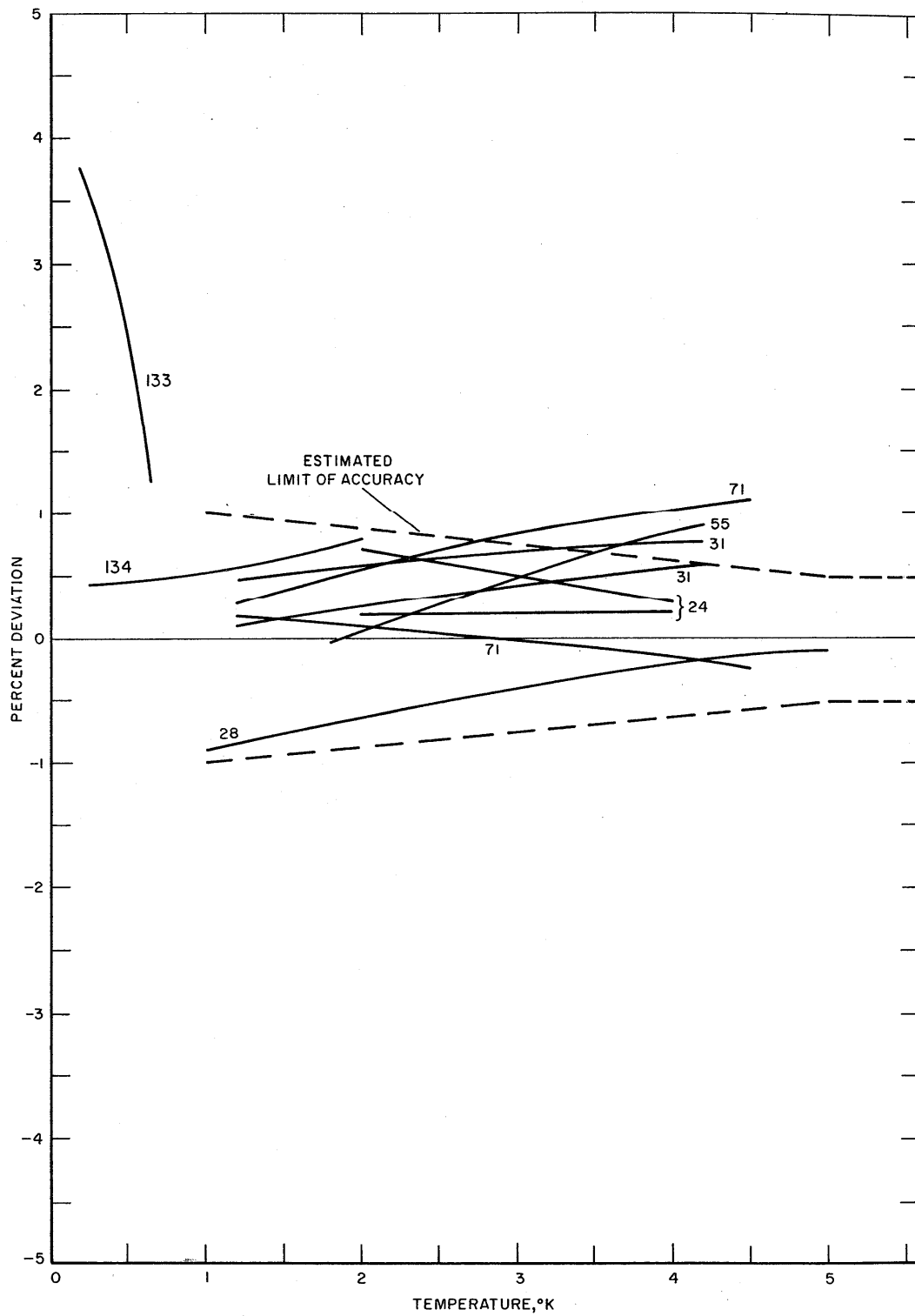
FIGURE 2c.1. *Deviations of the heat-capacity data of the literature on copper from the selected values in the range 0 to 5 °K and the estimated limit of accuracy of the selected values. (Set 1)*

17
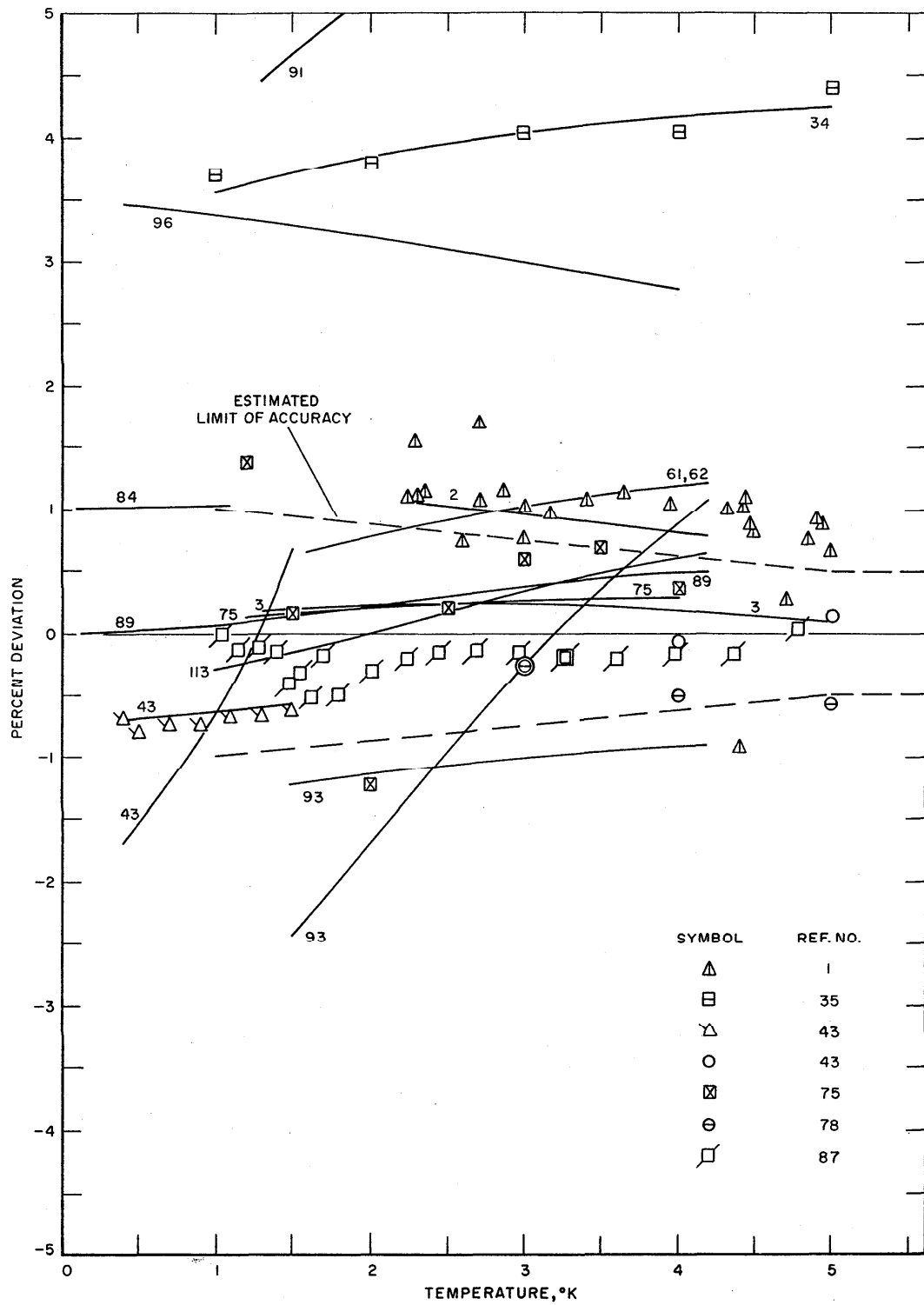
FIGURE 2c.2. *Deviations of the heat-capacity data of the literature on copper from the selected values in the range 0 to 5 °K and the estimated limit of accuracy of the selected values. (Set 2)*

18
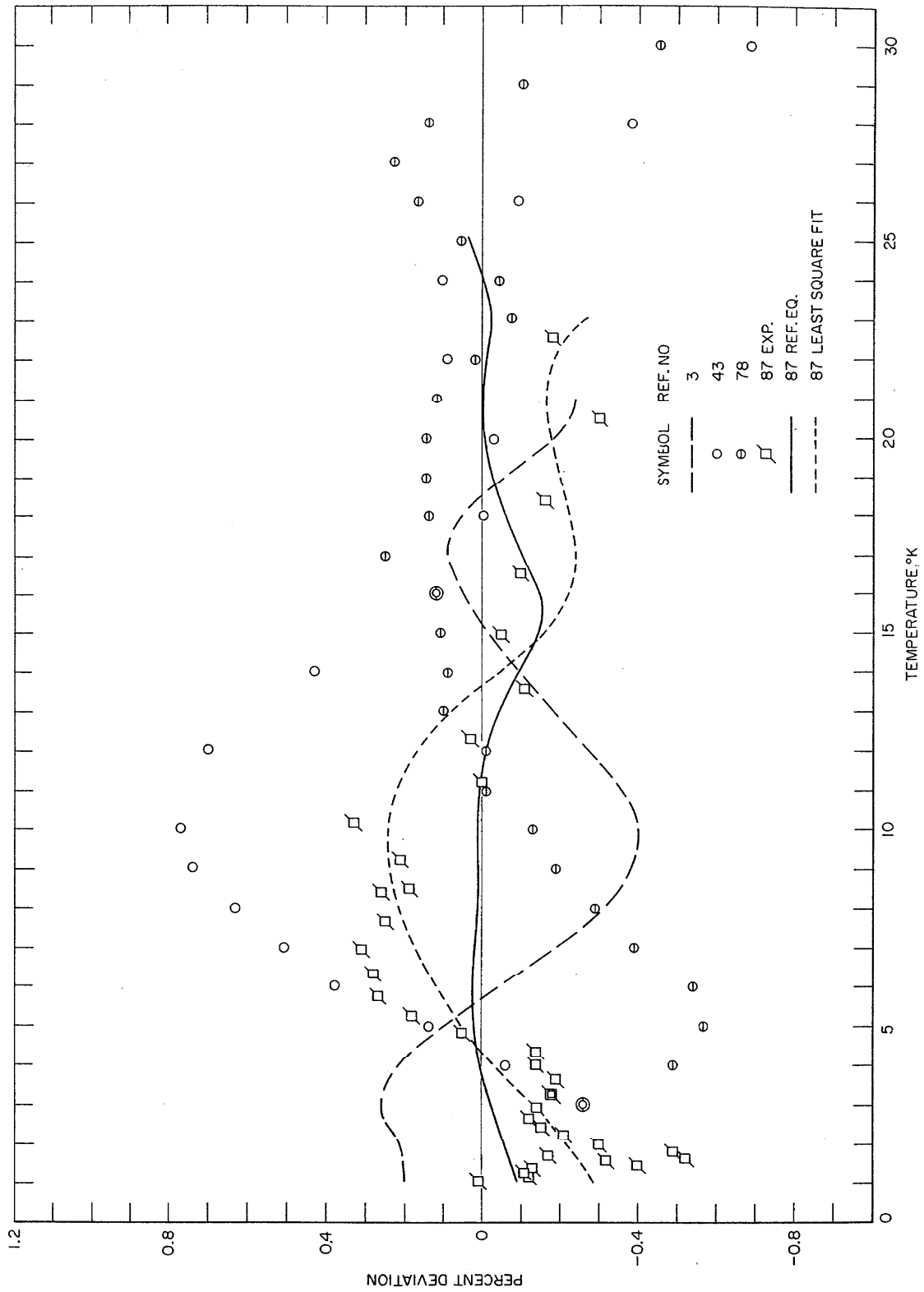
FIGURE 2d. *Comparison of some recently reported precise heat-capacity data on copper with the selected values in the range 0 to 30 °K.*

TABLE 2. *Thermodynamic Functions for Copper*

Gram atomic wt.=63.5400, $T$ °K=273.15+$t$ °C, 1 cal=4.1840$J$

| $T$ | $C_P^o$ | $H_T^o-H_0^o$ | $(H_T^o-H_0^o)/T$ | $S_T^o$ | $-(G_T^o-H_0^o)$ | $-(G_T^o-H_0^o)/T$ |
|---|---|---|---|---|---|---|
| °K | J/deg-mol | J/mol | J/deg-mol | J/deg-mol | J/mol | J/deg-mol |
| 1.00 | 0.000743 | 0.000359 | 0.000359 | 0.000711 | 0.000351 | 0.000351 |
| 2.00 | 0.00177 | 0.00158 | 0.000790 | 0.00152 | 0.00145 | 0.000727 |
| 3.00 | 0.00337 | 0.00409 | 0.00136 | 0.00251 | 0.00345 | 0.00115 |
| 4.00 | 0.00582 | 0.00860 | 0.00215 | 0.00379 | 0.00657 | 0.00164 |
| 5.00 | 0.00943 | 0.0161 | 0.00322 | 0.00546 | 0.0112 | 0.00223 |
| 6.00 | 0.0145 | 0.0279 | 0.00466 | 0.00760 | 0.0176 | 0.00294 |
| 7.00 | 0.0213 | 0.0456 | 0.00652 | 0.0103 | 0.0265 | 0.00379 |
| 8.00 | 0.0301 | 0.0712 | 0.00889 | 0.0137 | 0.0385 | 0.00481 |
| 9.00 | 0.0414 | 0.107 | 0.0119 | 0.0179 | 0.0542 | 0.00602 |
| 10.00 | 0.0555 | 0.155 | 0.0155 | 0.0229 | 0.0746 | 0.00746 |
| 11.00 | 0.0727 | 0.219 | 0.0199 | 0.0290 | 0.100 | 0.00913 |
| 12.00 | 0.0936 | 0.302 | 0.0251 | 0.0362 | 0.133 | 0.0111 |
| 13.00 | 0.119 | 0.407 | 0.0313 | 0.0447 | 0.173 | 0.0133 |
| 14.00 | 0.149 | 0.541 | 0.0386 | 0.0545 | 0.223 | 0.0159 |
| 15.00 | 0.184 | 0.706 | 0.0471 | 0.0660 | 0.283 | 0.0189 |
| 16.00 | 0.225 | 0.910 | 0.0569 | 0.0791 | 0.355 | 0.0222 |
| 17.00 | 0.273 | 1.158 | 0.0681 | 0.0941 | 0.442 | 0.0260 |
| 18.00 | 0.328 | 1.458 | 0.0810 | 0.111 | 0.544 | 0.0302 |
| 19.00 | 0.390 | 1.816 | 0.0956 | 0.131 | 0.665 | 0.0350 |
| 20.00 | 0.462 | 2.242 | 0.112 | 0.152 | 0.806 | 0.0403 |
| 25.00 | 0.963 | 5.703 | 0.228 | 0.305 | 1.917 | 0.0767 |
| 30.00 | 1.693 | 12.25 | 0.408 | 0.541 | 3.995 | 0.133 |
| 35.00 | 2.638 | 22.99 | 0.657 | 0.871 | 7.487 | 0.214 |
| 40.00 | 3.740 | 38.89 | 0.972 | 1.294 | 12.86 | 0.322 |
| 45.00 | 4.928 | 60.54 | 1.345 | 1.802 | 20.57 | 0.457 |
| 50.00 | 6.154 | 88.23 | 1.765 | 2.385 | 31.01 | 0.620 |
| 55.00 | 7.385 | 122.1 | 2.220 | 3.029 | 44.52 | 0.809 |
| 60.00 | 8.595 | 162.0 | 2.701 | 3.724 | 61.38 | 1.023 |
| 65.00 | 9.759 | 208.0 | 3.199 | 4.458 | 81.82 | 1.259 |
| 70.00 | 10.86 | 259.5 | 3.708 | 5.222 | 106.0 | 1.514 |
| 75.00 | 11.89 | 316.4 | 4.219 | 6.007 | 134.1 | 1.788 |
| 80.00 | 12.85 | 378.4 | 4.729 | 6.806 | 166.1 | 2.076 |
| 85.00 | 13.74 | 444.9 | 5.234 | 7.612 | 202.1 | 2.378 |
| 90.00 | 14.56 | 515.7 | 5.730 | 8.421 | 242.2 | 2.691 |
| 95.00 | 15.31 | 590.4 | 6.215 | 9.229 | 286.4 | 3.014 |
| 100.00 | 16.01 | 668.7 | 6.687 | 10.03 | 334.5 | 3.345 |
| 105.00 | 16.64 | 750.3 | 7.146 | 10.83 | 386.7 | 3.683 |
| 110.00 | 17.22 | 835.0 | 7.591 | 11.62 | 442.8 | 4.025 |
| 115.00 | 17.76 | 922.5 | 8.021 | 12.39 | 502.8 | 4.372 |
| 120.00 | 18.25 | 1013. | 8.438 | 13.16 | 566.7 | 4.723 |
| 125.00 | 18.70 | 1105. | 8.839 | 13.91 | 634.4 | 5.075 |
| 130.00 | 19.12 | 1199. | 9.227 | 14.66 | 705.8 | 5.429 |
| 135.00 | 19.51 | 1296. | 9.601 | 15.39 | 780.9 | 5.785 |
| 140.00 | 19.87 | 1395. | 9.961 | 16.10 | 859.7 | 6.140 |
| 145.00 | 20.20 | 1495. | 10.31 | 16.80 | 941.9 | 6.496 |
| 150.00 | 20.51 | 1597. | 10.64 | 17.49 | 1028. | 6.851 |
| 155.00 | 20.79 | 1700. | 10.97 | 18.17 | 1117. | 7.206 |
| 160.00 | 21.05 | 1804. | 11.28 | 18.84 | 1209. | 7.559 |
| 165.00 | 21.30 | 1910. | 11.58 | 19.49 | 1305. | 7.910 |
| 170.00 | 21.53 | 2017. | 11.87 | 20.13 | 1404. | 8.260 |

20

TABLE 2. *Thermodynamic Functions for Copper* — Continued

Gram atomic wt.=63.5400, $T\,°K=273.15+t\,°C$, 1 cal=4.1840 $J$

| $T$ | $C_P^\circ$ | $H_T^\circ-H_0^\circ$ | $(H_T^\circ-H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ-H_0^\circ)$ | $-(G_T^\circ-H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | J/deg-mol | J/mol | J/deg-mol | J/deg-mol | J/mol | J/deg-mol |
| 175.00 | 21.74 | 2125. | 12.15 | 20.75 | 1506. | 8.608 |
| 180.00 | 21.94 | 2235. | 12.42 | 21.37 | 1612. | 8.954 |
| 185.00 | 22.13 | 2345. | 12.68 | 21.97 | 1720. | 9.298 |
| 190.00 | 22.31 | 2456. | 12.93 | 22.57 | 1831. | 9.639 |
| 195.00 | 22.47 | 2568. | 13.17 | 23.15 | 1946. | 9.978 |
| 200.00 | 22.63 | 2681. | 13.40 | 23.72 | 2063. | 10.31 |
| 205.00 | 22.77 | 2794. | 13.63 | 24.28 | 2183. | 10.65 |
| 210.00 | 22.91 | 2908. | 13.85 | 24.83 | 2306. | 10.98 |
| 215.00 | 23.04 | 3023. | 14.06 | 25.37 | 2431. | 11.31 |
| 220.00 | 23.17 | 3139. | 14.27 | 25.90 | 2559. | 11.63 |
| 225.00 | 23.28 | 3255. | 14.47 | 26.42 | 2690. | 11.96 |
| 230.00 | 23.39 | 3372. | 14.66 | 26.94 | 2824. | 12.28 |
| 235.00 | 23.50 | 3489. | 14.85 | 27.44 | 2960. | 12.59 |
| 240.00 | 23.60 | 3607. | 15.03 | 27.94 | 3098. | 12.91 |
| 245.00 | 23.69 | 3725. | 15.20 | 28.42 | 3239. | 13.22 |
| 250.00 | 23.78 | 3844. | 15.37 | 28.90 | 3382. | 13.53 |
| 255.00 | 23.86 | 3963. | 15.54 | 29.37 | 3528. | 13.83 |
| 260.00 | 23.94 | 4082. | 15.70 | 29.84 | 3676. | 14.14 |
| 265.00 | 24.02 | 4202. | 15.86 | 30.30 | 3826. | 14.44 |
| 270.00 | 24.09 | 4322. | 16.01 | 30.75 | 3979. | 14.74 |
| 273.15 | 24.13 | 4398. | 16.10 | 31.02 | 4076. | 14.92 |
| 275.00 | 24.15 | 4443. | 16.16 | 31.19 | 4134. | 15.03 |
| 280.00 | 24.22 | 4564. | 16.30 | 31.62 | 4291. | 15.32 |
| 285.00 | 24.28 | 4685. | 16.44 | 32.05 | 4450. | 15.61 |
| 290.00 | 24.34 | 4807. | 16.57 | 32.48 | 4611. | 15.90 |
| 295.00 | 24.40 | 4929. | 16.71 | 32.89 | 4775. | 16.19 |
| 298.15 | 24.44 | 5005. | 16.79 | 33.15 | 4879. | 16.36 |
| 300.00 | 24.46 | 5051. | 16.84 | 33.30 | 4940. | 16.47 |

$H_0^\circ$ is the enthalpy of the solid at 0 °K and 1 atm pressure.

## 4.2. Silver (Ag, 107.870), Assessment of the Data Sources

There seems to have been relatively little interest in the heat capacity of silver prior to 1952. The final selected values of heat capacity above 30 °K are based on those reported by Griffiths and Griffiths [120, 121, 122, 123]; Eucken, Clusius, and Woitinek [40]; Bronson and Wilson [16]; and Meads, Forsythe, and Giauque [81]. Between 5 and 30 °K, the data reported by Martin [78] and by Ahlers [4] were given the most weight. Below 5 °K most of the published data were used in obtaining the selected values. The data of Keesom and Kok [69, 70] and Ramanathan and Srinivasan [91] were not given any weight.

Griffiths and Griffiths [120, 121, 122, 123] reported six measurements in the interval from 158 to 371 °K on a sample of 99.99 percent purity. A gas-filled isothermal-shield type calorimeter was used in conjunction with a platinum-resistance thermometer calibrated in close accordance with the present definition of the IPTS [106]. The values reported at 158 and 187 °K are more than 1 percent higher than the selected values. The other values at the higher temperatures are within ±0.2 percent of the selected and expected values.

Eucken, Clusius, and Woitinek [40] measured a sample of 99.99 percent purity in the range 11 to 205 °K by means of an isothermal-shield calorimeter. The temperatures were determined by means of a Pb-resistance thermometer. Above 20 °K their values are generally within ±1 percent of the selected values, but below 20 °K they deviate positively as much as 8 percent.

Mendelssohn and Closs [129] reported measurements from 2 to 20 °K. The observations are presented graphically only. The average Debye characteristic temperature given as 210 °K is expected to be low since the electronic contribution was not taken into account.

Keesom and Kok reported two sets of measurements on samples of equal purity (99.95+ percent) in the ranges 1.4 to 20.3 °K (1932) [69] and 1.7 to

21

4.9 (1934) [70]. In the first set helium exchange gas was used for cooling and in the second a mechanical heat switch was used. The two results below about 5 °K scatter more than 25 percent. The precision of the data above 5 °K is better, but the values are as much as 9 percent higher than the selected values. No weight was given to their data.

Bronson and Wilson [16] used a non-vacuum type adiabatic calorimeter to determine the heat capacity of a sample of 99.98+ percent purity from $-80$ to $+120$ °C (193 to 393 °K). The impurities were Cu: 0.0095 and Fe: 0.0018 percent. The temperature of the specimen was determined indirectly by measuring the temperature of the relatively massive adiabatic shield by means of a platinum-resistance thermometer when thermocouples indicated the specimen and the shield to be at the same temperature. Smoothed values were reported. The values obtained from a smooth curve through the observed values and those calculated from an equation fitted to the observed values are shown to agree within 0.005 percent. Their values are consistently lower than the selected values, the maximum deviation being $-0.4$ percent.

Moser [83] made measurements on a sample of 99.99 percent purity from 52 to 652 °C (325 to 925 °K) by means of a vacuum-adiabatic calorimeter operated by a continuous heating method. The temperatures were measured by means of silver-constantan thermocouples calibrated against a platinum-resistance thermometer. These higher temperature values of heat capacity were used primarily to decide on the values in the region of 300 °K and are, therefore, not shown in figure 4a. Moser's values tended to be relatively low in the range up to 450 °K.

Meads, Forsythe, and Giauque [81] made measurements on a single crystal of 99.99 percent purity. The sample was melted and crystallized in an atmosphere of nitrogen. Measurements made in the years 1931 to 1939 are reported. The initial series of measurements made in 1931 soon after the sample preparation was found to disagree in the range 15 to 25 °K with measurements made in 1935 and 1939. The sample was considered to have changed with time, consequently the material was remelted and recrystallized in vacuum. Measurements made soon after on this material agreed with the 1935 and 1939 measurements. No further explanation is given for the discrepancy in the 1931 measurements. Their values above 50 °K are generally higher than the selected values, with the maximum deviation of about $+1.2$ percent at 290 °K. Between 30 and 50 °K their values are mostly lower (maximum deviation being $-1$ percent) and below 30 °K mostly higher (maximum deviation being $+7$ percent) than the selected values.

Mustajoki [130] reported measurements on a sample of 99.96 percent purity from 339 to 758 °K (66 to 485 °C) using a vacuum-adiabatic continuous-heating method. Silver-constantan thermocouples were used for the temperature measurements. Up to the temperature of interest (450 °K), the observations are about 0.5 percent lower than the expected values. The data were used mainly to select the best values of heat capacity in the region of 300 °K.

Keesom and Pearlman [65, 66] made measurements between 1.2 and 4.2 °K on a single-crystal sample of 99.999 percent purity. The first paper [65] showed anomalies that were subsequently attributed to deviations of the 1948 $^4$He temperature scale [112, 98] from the thermodynamic scale. In the second paper [66] the authors showed that when the 1948 $^4$He scale was adjusted to conform more nearly to the thermodynamic scale the anomalies disappeared [38]. The values of $\gamma$ and $\theta_D(0)$ used in the analysis were from the latter publication. The value of $\gamma$ is the highest among a cluster of values, while the value of $\theta_D(0)$ is the lowest among a cluster of values. Their values of heat capacity are about 1.5 percent higher than the selected values.

Three sets of measurements have been reported by Hoare, Matthews, and Walling [57]; Hoare and Yates [58]; and Dixon, Hoare, Holden, and Moody [31]. No numerical values were given for silver in the first paper [57]. In the second paper [58] $\gamma$ and $\theta_D(0)$ obtained from measurements between 2 and 4.2 °K were reported, and the values of heat capacity calculated from them deviate negatively from $-0.2$ percent at 2 °K to $-4.2$ percent at 4.2 °K. In the third paper [31] the results were reported on two series of measurements on a spectrographically pure sample. The 1958 $^4$He scale [14] was used. The results of $\gamma$ and $\theta_D(0)$ reported for the two series of measurements do not quite overlap within the precision figures given. The values of heat capacity calculated from the $\gamma$ and $\theta_D(0)$ agree with each other within 0.7 percent and are within about 0.6 percent of the selected values.

Rayne [133] reported measurements on a sample of 99.9+ percent purity from 0.2 to 1 °K. (See the section on copper under reference [133] for a brief description of the experimental method used.) No numerical observations are given in the paper. The lattice contribution was considered negligible and the electronic coefficient of the heat capacity, $\gamma$, based on the observations between 0.2 and 0.65 °K is given. The value of $\gamma$ reported $(0.669 \pm 0.063$ mJ °K$^{-2}$ mol$^{-1}$) is higher than most of the recently published values. The values of electronic heat capacity based on the above value of $\gamma$ are higher than the selected values based on both electronic and lattice contributions below 0.4 °K but lower above this temperature. This is to be expected since the lattice contribution is significant at these temperatures. (The lattice contribution in the present analysis has been found to be about 1 percent at 0.2 °K.)

Corak, Garfunkel, Satterthwaite, and Wexler [28] made measurements from 1 to 5 °K on an annealed sample of 99.999+ percent purity. Cooling was done by helium exchange gas. The tem-

peratures were determined by means of a carbon-resistance thermometer calibrated on the 1948 $^4$He scale [112, 98] and adjusted for the deviations of the scale from the thermodynamic scale [38, 9]. Their value of $\gamma$ is the lowest of those published and that of $\theta_D(0)$ is within a cluster of values published. Their values of heat capacity are in general lower than the selected values, 5 percent lower at 1 °K and converging at 5 °K.

Rayne [94] measured from 1.5 to 4.2 °K a sample of 99.99 percent purity using a mechanical heat switch for cooling. A carbon-resistance thermometer was used that was calibrated on the 1948 $^4$He scale [112, 98] with adjustments made for deviations from the thermodynamic scale [38]. The value of $\gamma$ obtained is low but that of $\theta_D(0)$ is in good agreement with other published values. His values of heat capacity are about 1 to 4 percent lower than the selected values.

Ramanathan and Srinivasan [91] made measurements on an annealed sample of purity higher than 99.7 percent from 1.3 to 4.2 °K. A mechanical heat switch was used for cooling. The values of $\gamma$ and $\theta_D(0)$ reported are relatively low. The 1948 $^4$He scale [112, 98] was used. No weight was given to the measurements in the final evaluation of the best values of heat capacity.

Filby and Martin [42] made three series of measurements from 0.4 to 1.5 °K on an annealed 99.9999 percent pure sample. The temperatures were based on $^3$He vapor pressure reported by Sydoriak and Roberts [107]. A superconducting Pb-wire heat switch was used for cooling. The three values of $\gamma$ obtained are among a cluster of recently published values; one of the values of $\theta_D(0)$ lies within a cluster of published values but the other two are located outside the cluster. The values of heat capacity from $\gamma=0.652$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0)=226.5$ °K range from $+0.2$ to $-0.1$ percent of the selected values. The values of heat capacity from the other two sets of $\gamma$ and $\theta_D(0)$ are on the average about 1 percent lower than the selected values.

Another series of measurements was reported by Martin [78] using a different calorimeter in the range 3 to 30 °K on a sample of the same purity. Germanium-resistance thermometers were used that had been calibrated on the 1958 $^4$He scale [14], on the vapor pressure of hydrogen [116], a gas thermometer [44], and the NBS–1955 provisional scale [60, 46]. The cooling was achieved by circulating helium between the heat sink and the sample through a separate small diameter tubing and subsequently removing the helium by pumping. The average value of $\gamma$ reported earlier by Filby and Martin [42] was used to calculate $\theta_D(T)$ from the experimental data. The reported value of $\theta_D(0)$, estimated from the values of $\theta_D(T)$, is in a cluster of recently published values and is in close agreement with the value reported earlier by Filby and Martin [42] in the same cluster. Martin's [78] values of heat capacity are well within 0.8 percent of the selected values.

DuChatenier and DeNobel [34, 35] reported measurements from 1 to 30 °K on a polycrystalline sample of 99.9999 percent purity. The only detectable impurities were 0.1 to 0.2 ppm of Cu, Pb, and Bi. The temperatures were based on the 1958 $^4$He scale [14] and the hydrogen vapor pressure work of Hoge and Arnold [59]. Helium exchange gas was used in cooling. The relatively high values of $\gamma$ and $\theta_D(0)$ reported are consistent with possible heat of desorption effect of helium at the lower temperatures. Their smoothed values of heat capacity show systematic "sinusoidal" deviations of $+3.5$ to $-2.5$ percent from the selected values. Similar deviations have been found with their data on copper and gold [34, 35, 36].

Green and Culbert [53], Green and Valladares [54], and Green [52], using the same or essentially the same apparatus, have reported within a period of little over a year four sets of measurements between 2 and 4 °K on polycrystalline annealed samples of 99.9999 percent purity. The sample indicated as 99.9999 (II) by Green [52] was borrowed from Isaacs and Massalski [62, 79] and was also 99.9999+ percent pure but from a different source of manufacture than the other three samples [52, 53, 54]. The 1958 $^4$He scale [14] was used in the four sets of measurements. (See the section on copper for a description of the unique "adiabatic" technique used by Green et al. [24, 52, 53, 54, 115].) Among the four reported values of $\theta_D(0)$ the maximum deviation is 0.4° in about 225 °K. The maximum deviation in the electronic heat-capacity coefficient $\gamma$ is 0.008 in about 0.650 mJ °K$^{-2}$ mol$^{-1}$. Isaacs and Massalski [61, 79, 101] reported on sample 99.9999(II), $\gamma=0.645\pm0.007$ mJ °K$^{-2}$ mol$^{-1}$ and $\theta_D(0)=228.9\pm2.0$ °K, based on the equation $C=\gamma T+AT^3+BT^5$. The values of $\gamma$ and $\theta_D(0)$ obtained by Green [52] on his sample (99.9999(I)) are 0.652 mJ °K$^{-2}$ mol$^{-1}$ and 225.4 °K, respectively, and on the sample of Isaacs and Massalski [61, 79] (99.9999(II)) are 0.651 mJ °K$^{-2}$ mol$^{-1}$ and 225.7 °K, respectively. These results indicate that the two samples, although they are from different sources of manufacture, are pure enough that the heat capacities are essentially the same within the capability of the experimental method. The values of heat capacity obtained by Green et al. [52, 53, 54] are all within 0.7 percent of the selected values, three sets being within 0.5 percent.

Massalski and Isaacs [61, 79, 101] made measurements between 1.6 and 4.2 °K on a polycrystalline sample of 99.9999+ purity using a calorimeter with a mechanical heat switch. A carbon-resistance thermometer was used that was calibrated on the 1958 $^4$He scale [14]. Isaacs [61] showed that a heat-capacity equation of the form:

$$C/T=\gamma+AT^2+BT^4$$

represented his data on silver better. The coefficient for the $T^4$ term obtained by the method of

23

least squares fitting of the observations to the equation is $0.00094 \pm 0.00008$ mJ $°K^{-6}$ mol$^{-1}$ [61].

In a recent private communication, Isaacs [62] showed a recalculation of the earlier data [61, 63, 79]. The equation obtained for silver is

$$C/T = (6.45 \pm 0.06) \times 10^{-4} + (1.677 \pm 0.006) \times 10^{-4} T^2$$

$$J \ °K^{-2} \ mol^{-1},$$

which no longer contains the $T^4$ term. The values of heat capacity calculated from the new equation deviate on the average about $-0.5$ percent from the selected values while the earlier values [61, 63] deviate as much as $+4.5$ percent.

Shinozaki and Arrott [105] reported measurements between 2 and 4 °K on a silver sample for which no information on purity or heat treatment is given. Carbon-resistance thermometers cali-

brated against the 1958 $^4$He scale [14] were used. A mechanical heat switch was used for cooling. The heat capacities calculated using their reported values of $\gamma$ and $\theta_D(0)$ are about 1 percent higher than the selected values.

Ahlers [4] reported measurements on a silver sample of 99.9999 percent purity from 1.4 to 26 °K. The germanium-resistance thermometer used was calibrated against the 1958 $^4$He scale [14], another germanium thermometer that was calibrated against a gas thermometer [87], vapor pressure of $H_2$ [116, 59], and the NBS–1955 scale [60, 46]. Contrary to the observations of Isaacs [61], the results below 6 °K were shown to be representable, within the root-mean-square deviation of 0.15 percent, by $C = AT + BT^3$ form of equation. The $T^5$ term was not needed. Ahler's [4] values of heat capacity are very close to the selected values, on the average within $-0.2$ percent.

TABLE 3. *Sources of heat-capacity data on silver used in the analysis*

| Year | Temperature range of heat measurements °K | Purity of specimen Weight % | Electronic coefficient, γ mJ °K⁻² mol⁻¹ × 10³ | Debye θ at 0 °K °K | Entropy at 298.15 °K J °K⁻¹ mol⁻¹ | cal °K⁻¹ mol⁻¹ | Calorimeter design | Thermometer | Temperature scale | Cooling of sample | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1914 | 158–371 | 99.99 | (Measurements were made at six temperatures) | | | | GI–I[e] | PRT[e] | IPTS[e] | gas[e] | [120, 121, 122, 123] |
| 1931 | 11–205 | 99.99 | | 210 | 42.51 | 10.16 | VI–I | Pb | Pb, vp-H₂, vp-O₂, gas, Pt | gas | [40] |
| 1932 | 2–20 | ? | | 210 | | | VI–I | gas | gas | gas | [129] |
| 1932 | 1.4–20.3 | 99.95+ | | | | | VI–I | phosphor-bronze, constantan | vp-He, vp-H₂, gas | gas | [69] |
| 1934 | 1.7–4.9 | 99.95+ | | | | | VI–I | phosphor-bronze, constantan | vp-He, gas | MHS | [70] |
| 1936 | 193–393 | 99.98+ | | | | | GA–I | TC, PRT | ITS | gas | [16] |
| 1936 | 325–925 | 99.99 | | | | | VA–C | TC | ITS | | [83] |
| 1941 | 15–298 | 99.99 (single crystal) | | | 42.70 | 10.21 | VI–I | Au-Ag | TC, vp-H₂, vp-O₂, gas | gas | [81] |
| 1952 | 1.2–4.2 | 99.999 (single crystal) | 660 | 225 | | | VI–I | | 1948 ⁴He 1955K ⁴He | | [65, 66] |
| 1953 | 10–20 | spectroscopically standardized | (No numerical data are given in the paper) | | | | VI–I | PRT, constantan | vp-H₂ | gas | [57] |
| 1954 | 0.2–1 | 99.9+ | 669 ±63 [a] | | | | VI–I | MS | MS, 1948 ⁴He | gas, AD–MC | [133] |
| 1955 | 1–5 | 99.98 (annealed) | 610 ±5 [a] | 225.3 ±0.2 [a] | | | VI–I | C | 1948W ⁴He | gas | [28] |
| 1956 | 1.5–4.2 | 99.99 | 613 ±5 [a] | 226.2 ±0.3 [a] | | | VI–I | C | 1948R ⁴He | MHS | [94] |
| 1957 | 1.3–4.2 | 99.7+ (annealed) | 615 ±10 [a] | 219.4 ±0.5 [a] | | | VI–I | C | 1948 ⁴He | MHS | [91] |
| 1957 | 2–4.2 | spectroscopically standardized | 690 ±30 [a] | 231 ±1 [a] | | | VI–I | C | 1955L ⁴He | cond | [58] |
| 1962 | 0.4–1.5 | 99.9999 (annealed) | 652 ±5 [a] (Run 1) 638 ±7 [a] (Run 2) 649 ±8 [a] (Run 3) | 226.5 ±2.3 [a] (Run 1) 223.4 ±3.2 [a] (Run 2) 229.0 ±4.5 [a] (Run 3) | | | VI–I | C | SR-³He | SHS | [42] |
| 1962 | 1–30 | 99.9999 | 682 | 226.2 | | | VI–I | C | 1958 ⁴He, vp-H₂ | gas | [34, 35] |
| 1965 | 2–4 | 99.9999 (annealed) | 646 ±5 [a] | 225.5 ±0.5 [a] | | | VA–I | C | 1958 ⁴He | MHS | [53] |
| 1965 | 1.2–4.2 | spectroscopically pure | 647 ±2 [a] 653 ±4 [a] | 226.2 ±0.1 [a] (Run 1) 226.5 ±0.2 [a] (Run 2) | | | VI–I | C | 1958 ⁴He | MHS | [31] |
| 1965 | 1.6–4.2 | 99.9999+ | 645 ±7 [a, c] | 228.9 ±2.0 [b,c,d] | | | VI–I | C | 1958 ⁴He | MHS | [79, 61, 101, 62] |
| 1966 | 3–30 | 99.9999 (annealed) | 646 ±4 [a] | 226.6 ±1.0 [a] | | | VA–C | Ge | 1958 ⁴He, vp-H₂, gas, NBS–1955 | cond | [78] |
| 1966 | 2–4 | 99.9999 (annealed) | 654 ±2 [a] | 225.8 ±0.1 [a] | | | VA–I | C | 1958 ⁴He | MHS | [54] |
| 1966 | 2–4 | 99.9999 (I) | 652 | 225.4 | | | VA–I | C | 1958 ⁴He | MHS | [52] |
| 1966 | 2–4 | 99.9999 (II) | 651 | 225.7 | | | VA–I | C | 1958 ⁴He | MHS | [52] |
| 1966 | 2–4 | ? | 656 | 225.3 | | | VI–I | C | 1958 ⁴He | MHS | [105] |
| 1967 | 1.4–26 | 99.9999 | 645 | 226.0 | | | VI–I | Ge | 1958 ⁴He, vp-H₂, NBS–1955 gas | MHS | [4] |

[a] These figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the precision of the values given.

[b] These figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the estimated uncertainties in the values given.

[c] From the equation of the form: $C = \gamma T + AT^3 + BT^5$, where $A = 12\pi^4 R/5[\theta_D(0)]^3$.

[d] Isaacs [62] recalculated the experimental observations and found silver to fit $C = \gamma T + AT^3$ equation and $\gamma = 0.645 \pm 0.006$ mJ °K⁻² mol⁻¹ and $\theta_D(0) = 226.3 \pm 0.3$ °K.

[e] See section 2 for definitions of symbols and abbreviations used.

25
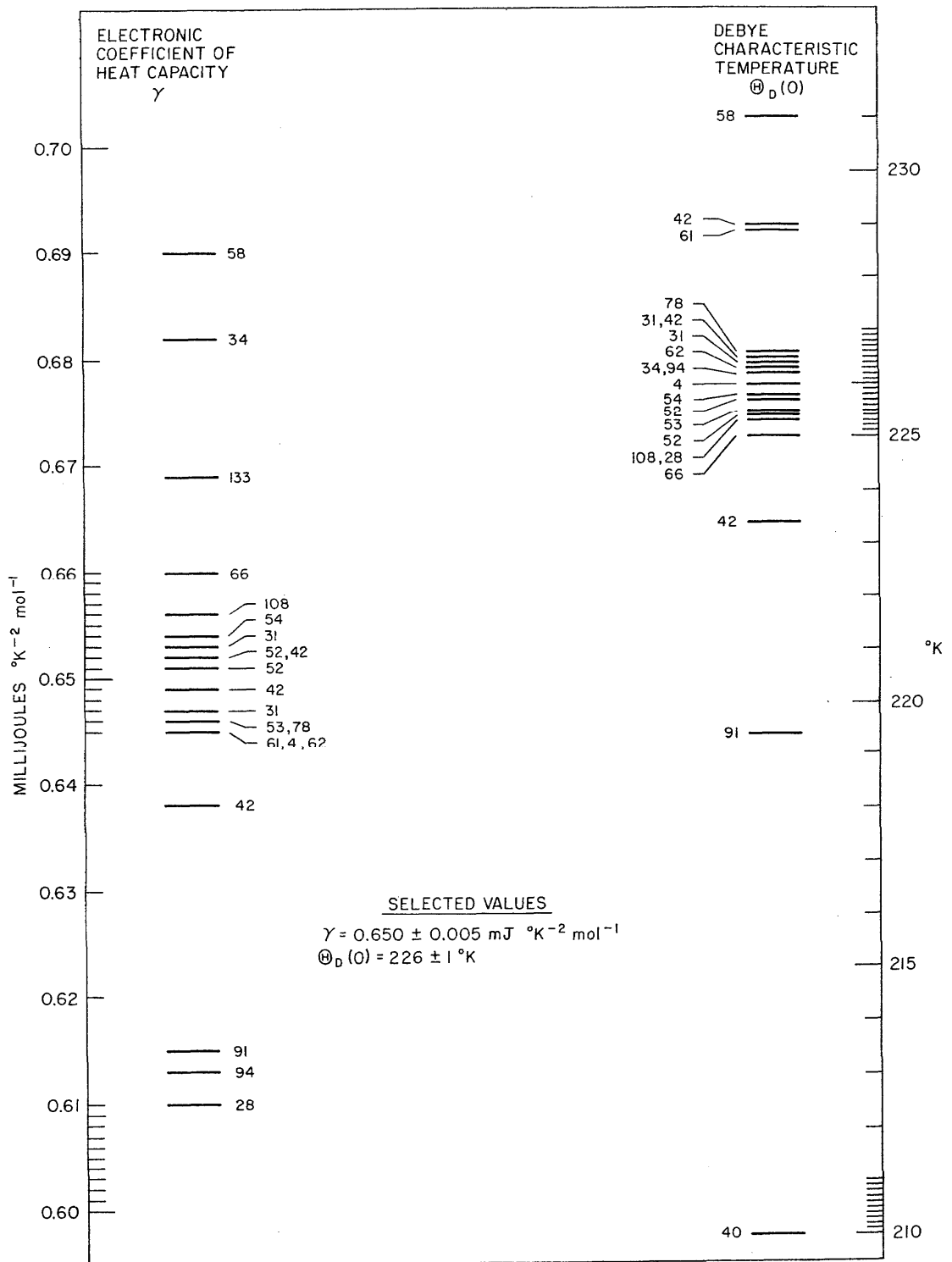
FIGURE 3.  *Comparison of the reported values of electronic coefficients of heat capacity,* $\gamma$, *and Debye characteristic temperatures,* $\theta_D(0)$, *of silver.*
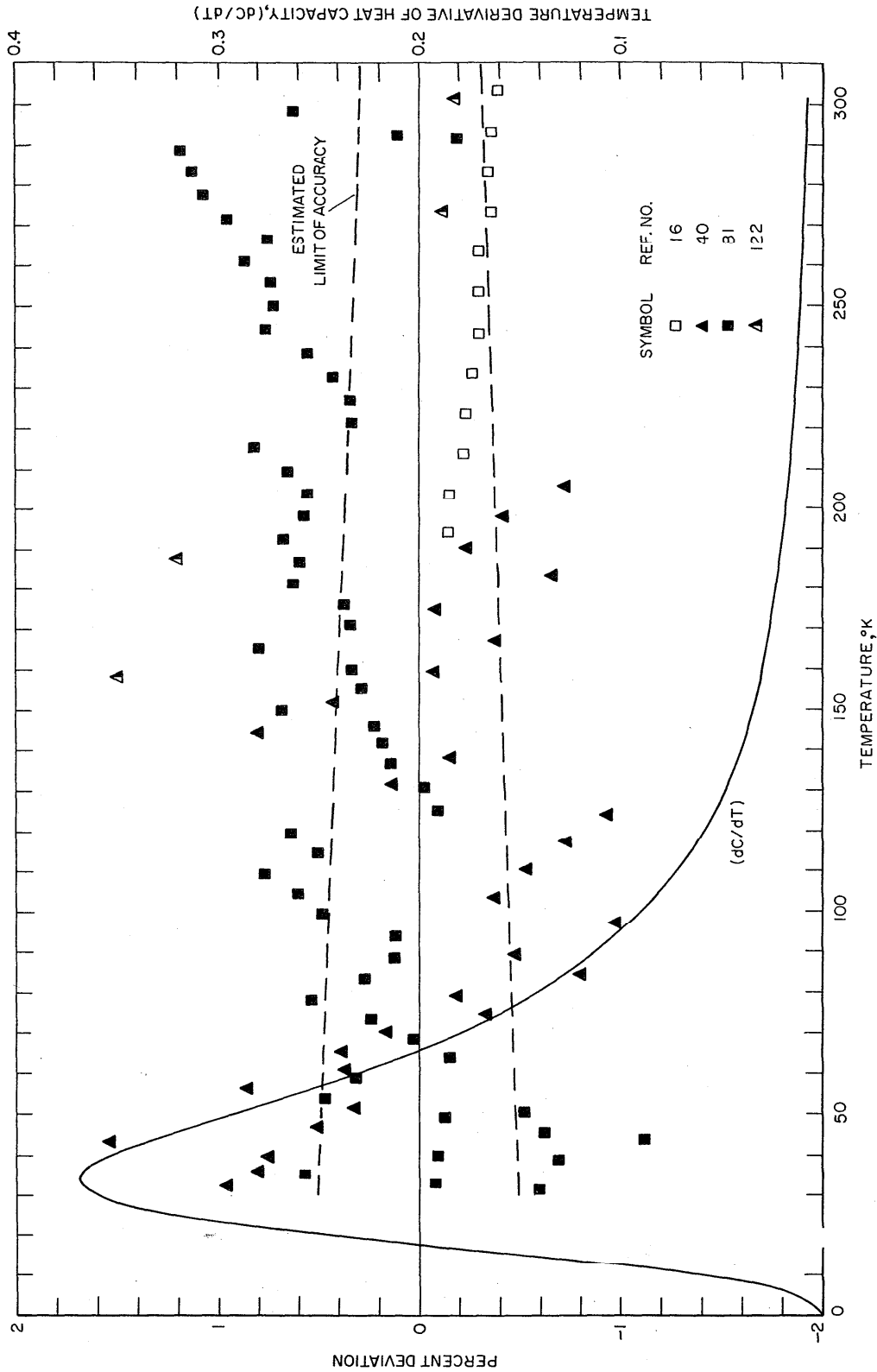
FIGURE 4a. Deviations of the heat-capacity data of the literature on silver from the selected values in the range 30 to 300 °K. The estimated limit of accuracy and the temperature derivative, $dC/dT$, in $J$ °$K^{-2}$ $mol^{-1}$ of the selected values.

27
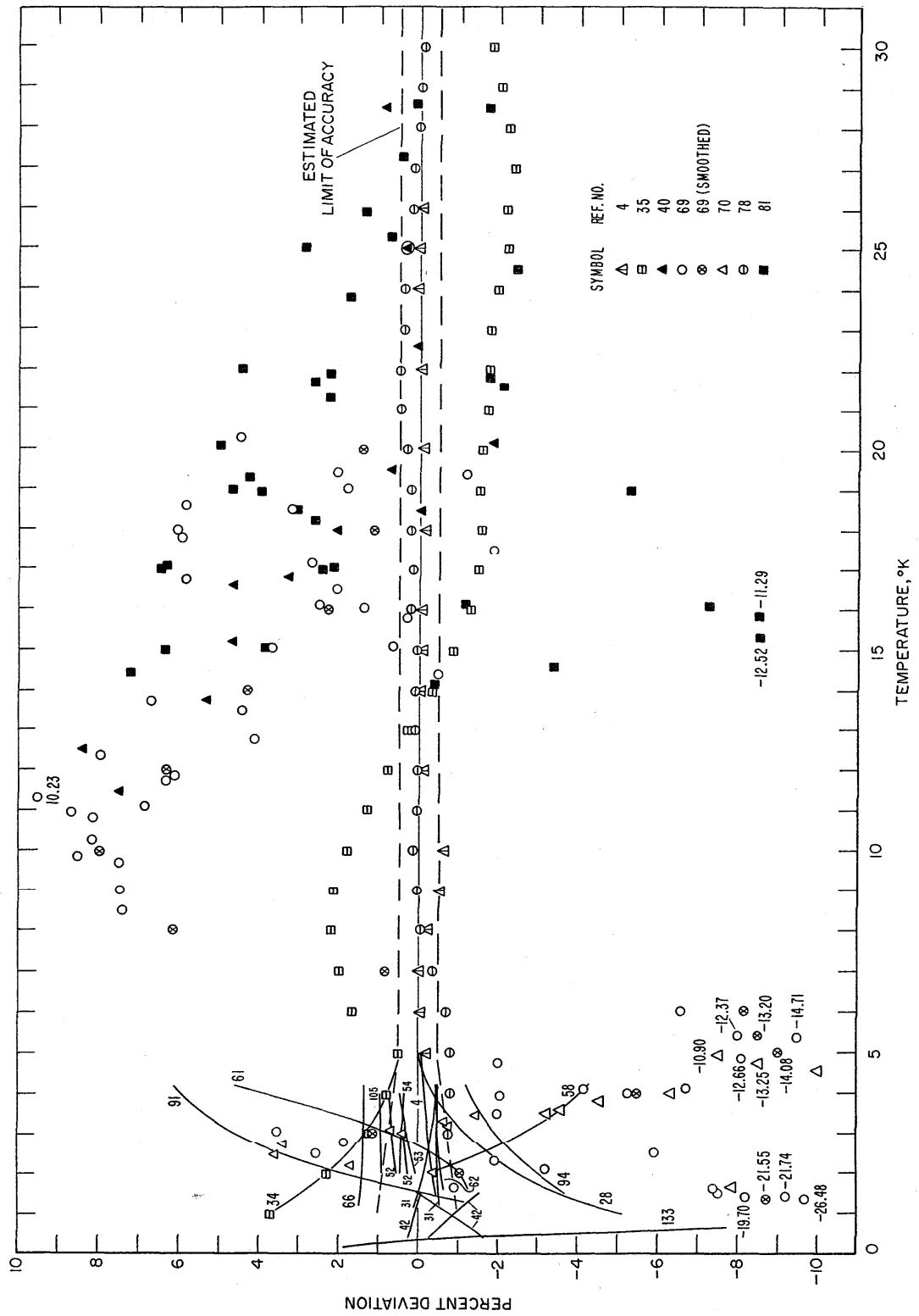
FIGURE 4b. *Deviations of the heat-capacity data of the literature on silver from the selected values in the range 0 to 30 °K and the estimated limit of accuracy of the selected values.*
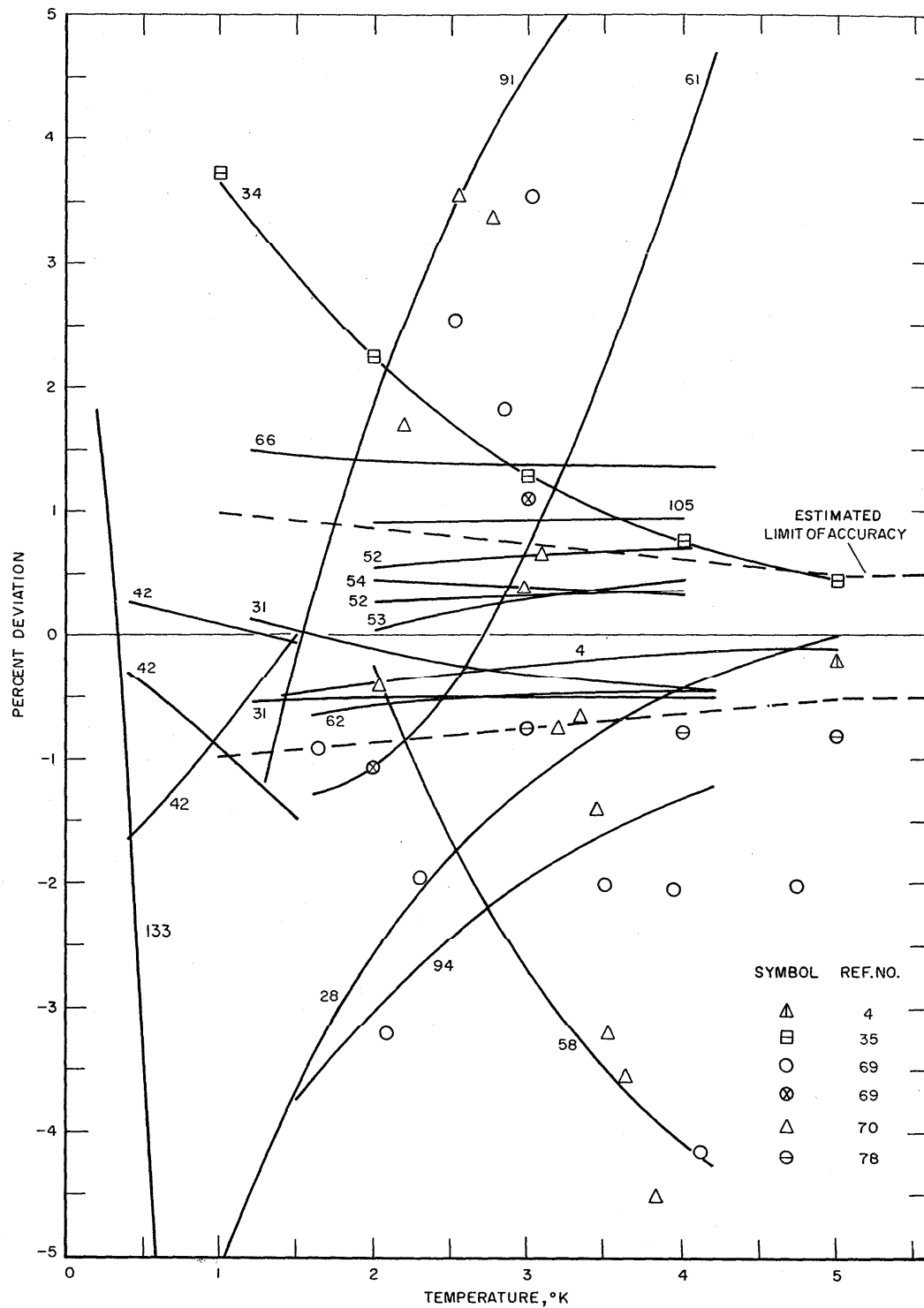
FIGURE 4c. *Deviations of the heat-capacity data of the literature on silver from the selected values in the range 0 to 5 °K and the estimated limit of accuracy of the selected values.*

29

TABLE 4. *Thermodynamic Functions for Silver*

Gram atomic wt.=107.8700, $T$ °K=273.15+$t$ °C, 1 cal=4.1840$J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | J/deg-mol | J/mol | J/deg-mol | J/deg-mol | J/mol | J/deg-mol |
| 1.00 | 0.000818 | 0.000367 | 0.000367 | 0.000706 | 0.000339 | 0.000339 |
| 2.00 | 0.00265 | 0.00197 | 0.000987 | 0.00175 | 0.00152 | 0.000762 |
| 3.00 | 0.00650 | 0.00633 | 0.00211 | 0.00347 | 0.00406 | 0.00135 |
| 4.00 | 0.0134 | 0.0160 | 0.00399 | 0.00619 | 0.00879 | 0.00220 |
| 5.00 | 0.0243 | 0.0344 | 0.00689 | 0.0103 | 0.0169 | 0.00338 |
| 6.00 | 0.0403 | 0.0663 | 0.0110 | 0.0160 | 0.0299 | 0.00498 |
| 7.00 | 0.0626 | 0.117 | 0.0167 | 0.0238 | 0.0496 | 0.00709 |
| 8.00 | 0.0927 | 0.194 | 0.0243 | 0.0341 | 0.0783 | 0.00979 |
| 9.00 | 0.132 | 0.306 | 0.0340 | 0.0472 | 0.119 | 0.0132 |
| 10.00 | 0.183 | 0.462 | 0.0462 | 0.0636 | 0.174 | 0.0174 |
| 11.00 | 0.247 | 0.676 | 0.0614 | 0.0839 | 0.247 | 0.0225 |
| 12.00 | 0.325 | 0.961 | 0.0801 | 0.109 | 0.343 | 0.0286 |
| 13.00 | 0.421 | 1.332 | 0.102 | 0.138 | 0.466 | 0.0359 |
| 14.00 | 0.535 | 1.809 | 0.129 | 0.174 | 0.622 | 0.0444 |
| 15.00 | 0.670 | 2.409 | 0.161 | 0.215 | 0.815 | 0.0544 |
| 16.00 | 0.826 | 3.155 | 0.197 | 0.263 | 1.054 | 0.0659 |
| 17.00 | 1.002 | 4.067 | 0.239 | 0.318 | 1.344 | 0.0790 |
| 18.00 | 1.199 | 5.166 | 0.287 | 0.381 | 1.693 | 0.0940 |
| 19.00 | 1.414 | 6.471 | 0.341 | 0.452 | 2.109 | 0.111 |
| 20.00 | 1.647 | 8.001 | 0.400 | 0.530 | 2.599 | 0.130 |
| 25.00 | 3.066 | 19.62 | 0.785 | 1.043 | 6.446 | 0.258 |
| 30.00 | 4.774 | 39.14 | 1.305 | 1.750 | 13.35 | 0.445 |
| 35.00 | 6.612 | 67.58 | 1.931 | 2.623 | 24.22 | 0.692 |
| 40.00 | 8.419 | 105.2 | 2.630 | 3.625 | 39.79 | 0.995 |
| 45.00 | 10.11 | 151.6 | 3.368 | 4.715 | 60.61 | 1.347 |
| 50.00 | 11.66 | 206.1 | 4.121 | 5.862 | 87.04 | 1.741 |
| 55.00 | 13.04 | 267.9 | 4.871 | 7.040 | 119.3 | 2.169 |
| 60.00 | 14.27 | 336.2 | 5.604 | 8.228 | 157.5 | 2.624 |
| 65.00 | 15.35 | 410.4 | 6.313 | 9.414 | 201.6 | 3.101 |
| 70.00 | 16.30 | 489.5 | 6.993 | 10.59 | 251.6 | 3.594 |
| 75.00 | 17.14 | 573.2 | 7.642 | 11.74 | 307.4 | 4.099 |
| 80.00 | 17.87 | 660.7 | 8.259 | 12.87 | 368.9 | 4.612 |
| 85.00 | 18.53 | 751.8 | 8.844 | 13.97 | 436.1 | 5.130 |
| 90.00 | 19.11 | 845.9 | 9.399 | 15.05 | 508.6 | 5.652 |
| 95.00 | 19.63 | 942.8 | 9.924 | 16.10 | 586.5 | 6.174 |
| 100.00 | 20.10 | 1042. | 10.42 | 17.12 | 669.6 | 6.696 |
| 105.00 | 20.52 | 1144. | 10.89 | 18.11 | 757.7 | 7.216 |
| 110.00 | 20.89 | 1247. | 11.34 | 19.07 | 850.6 | 7.733 |
| 115.00 | 21.23 | 1353. | 11.76 | 20.01 | 948.3 | 8.246 |
| 120.00 | 21.54 | 1460. | 12.16 | 20.92 | 1051. | 8.755 |
| 125.00 | 21.82 | 1568. | 12.54 | 21.80 | 1157. | 9.260 |
| 130.00 | 22.07 | 1678. | 12.91 | 22.66 | 1269. | 9.759 |
| 135.00 | 22.31 | 1789. | 13.25 | 23.50 | 1384. | 10.25 |
| 140.00 | 22.52 | 1901. | 13.58 | 24.32 | 1504. | 10.74 |
| 145.00 | 22.72 | 2014. | 13.89 | 25.11 | 1627. | 11.22 |
| 150.00 | 22.90 | 2128. | 14.19 | 25.88 | 1755. | 11.70 |
| 155.00 | 23.07 | 2243. | 14.47 | 26.64 | 1886. | 12.17 |
| 160.00 | 23.22 | 2358. | 14.74 | 27.37 | 2021. | 12.63 |
| 165.00 | 23.37 | 2475. | 15.00 | 28.09 | 2160. | 13.09 |
| 170.00 | 23.50 | 2592. | 15.25 | 28.79 | 2302. | 13.54 |

TABLE 4. *Thermodynamic Functions for Silver* — Continued

Gram atomic wt.=107.8700, $T$ °K=273.15+$t$ °C, 1 cal=4.1840$J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | J/deg-mol | J/mol | J/deg-mol | J/deg-mol | J/mol | J/deg-mol |
| 175.00 | 23.63 | 2710. | 15.49 | 29.47 | 2448. | 13.99 |
| 180.00 | 23.75 | 2828. | 15.71 | 30.14 | 2597. | 14.43 |
| 185.00 | 23.86 | 2947. | 15.93 | 30.79 | 2749. | 14.86 |
| 190.00 | 23.96 | 3067. | 16.14 | 31.43 | 2904. | 15.29 |
| 195.00 | 24.06 | 3187. | 16.34 | 32.05 | 3063. | 15.71 |
| 200.00 | 24.16 | 3308. | 16.54 | 32.66 | 3225. | 16.12 |
| 205.00 | 24.24 | 3429. | 16.72 | 33.26 | 3390. | 16.54 |
| 210.00 | 24.33 | 3550. | 16.90 | 33.85 | 3558. | 16.94 |
| 215.00 | 24.41 | 3672. | 17.08 | 34.42 | 3728. | 17.34 |
| 220.00 | 24.49 | 3794. | 17.25 | 34.98 | 3902. | 17.74 |
| 225.00 | 24.56 | 3917. | 17.41 | 35.53 | 4078. | 18.12 |
| 230.00 | 24.63 | 4040. | 17.56 | 36.07 | 4257. | 18.51 |
| 235.00 | 24.69 | 4163. | 17.71 | 36.60 | 4439. | 18.89 |
| 240.00 | 24.76 | 4287. | 17.86 | 37.12 | 4623. | 19.26 |
| 245.00 | 24.82 | 4411. | 18.00 | 37.63 | 4810. | 19.63 |
| 250.00 | 24.88 | 4535. | 18.14 | 38.14 | 4999. | 20.00 |
| 255.00 | 24.93 | 4659. | 18.27 | 38.63 | 5191. | 20.36 |
| 260.00 | 24.99 | 4784. | 18.40 | 39.11 | 5386. | 20.71 |
| 265.00 | 25.04 | 4909. | 18.53 | 39.59 | 5582. | 21.07 |
| 270.00 | 25.09 | 5035. | 18.65 | 40.06 | 5782. | 21.41 |
| 273.15 | 25.12 | 5114. | 18.72 | 40.35 | 5908. | 21.63 |
| 275.00 | 25.14 | 5160. | 18.76 | 40.52 | 5983. | 21.76 |
| 280.00 | 25.19 | 5286. | 18.88 | 40.97 | 6187. | 22.10 |
| 285.00 | 25.24 | 5412. | 18.99 | 41.42 | 6393. | 22.43 |
| 290.00 | 25.28 | 5538. | 19.10 | 41.86 | 6601. | 22.76 |
| 295.00 | 25.32 | 5665. | 19.20 | 42.29 | 6811. | 23.09 |
| 298.15 | 25.35 | 5745. | 19.27 | 42.56 | 6945. | 23.29 |
| 300.00 | 25.37 | 5792. | 19.31 | 42.72 | 7024. | 23.41 |

$H_0^\circ$ is the enthalpy of the solid at 0 °K and 1 atm pressure.

## 4.3. Gold (Au, 196.967), Assessment of the Data Sources

Since the measurements by Clusius and Harteck [25] in 1928, about a quarter century elapsed before Geballe and Giauque [48] made the next study on gold in 1952. Since 1952, however, many measurements have been reported, in particular below 20 °K.

The final selected values of heat capacity between 30 and 300 °K were based largely on the data reported by Geballe and Giauque [48] and by Franzosini and Clusius [45]. The earlier measurements of Clusius and Harteck [25] were given very little weight. The average deviation from the selected values of the data reported by Geballe and Giauque [48] and by Franzosini and Clusius [45] is about 0.2 percent, while the average deviation of the data reported by Clusius and Harteck [25] is about 1 percent.

Between 5 and 30 °K most weight was given to the data reported by Martin [78], the average deviation from the final selected values being less than 0.1 percent.

The equation of the form:

$$C = \gamma T + AT^3 + BT^5$$

is a better representation of the heat-capacity data for gold below 5 °K than the form $C = \gamma T + AT^3$. Most weight was given to the values of heat capacity corresponding to the three coefficients for the equation reported by Isaacs [101] and by Will and Green [115] and to those corresponding to the two coefficients for the equation of the form:

$$C = \gamma T + AT^3$$

reported by Martin [77, 78] for the measurements between 0.4 and 1.5 °K. Very little weight was given to papers in which the data between 1 and 5 °K

31

were fitted to the two-term equation. The values of heat capacity calculated using the $\gamma$ and $\theta_D(0)$ obtained with the two-term equation deviate from the selected values "parabolically". In the discussions dealing with each data source, percent deviations are given for the ends of the temperature range of measurements and at the "trough" of the deviation.

Clusius and Harteck [25] reported measurements between 15 and 212 °K on a sample described as "Feingold der Deutschen Goldscheideanstalt." Later Franzosini and Clusius [45] reported new measurements between 13 and 273 °K on a 99.99 percent pure sample. Isothermal-shield calorimeters were used in both sets of measurements. Below 30 °K the deviations of the data of Clusius and Harteck [25] from the selected values are within +6.5 and −2.5 percent and above 30 °K within +1.5 and −0.9 percent (average deviation = 1 percent). Below 30 °K the deviations of the data of Franzosini and Clusius [45] from the selected values are within +5 and −2.3 percent and above 30 °K within +0.8 and −0.5 percent (average deviation = 0.2 percent).

Geballe and Giauque [48] reported measurements between 16 and 309 °K on a single crystal (2.5 kg) of 99.99 percent purity. Analysis showed 0.001 percent each of Ag, Cu, and Fe. Gold-silver alloy wire, calibrated against a copper-constantan thermocouple temperature scale [49, 50], was used for temperature measurements. Their data were included in the selection of the best values of heat capacity. Below 30 °K their values of heat capacity do not deviate from the selected values by more than +2.5 and −2.0 percent and above 30 °K by more than +2 and −0.6 percent (average deviation = 0.2 percent).

Corak, Garfunkel, Satterthwaite, and Wexler [28] reported measurements from 1 to 5 °K on an annealed sample of 99.99+ percent purity. Cooling was achieved by helium exchange gas. A carbon-resistance thermometer was used that was calibrated on the 1948 $^4$He scale [112, 98] adjusted for deviations from the thermodynamic scale [38, 9]. The values of $\gamma$ and $\theta_D(0)$ reported are typical of those published using the two-term heat-capacity equation: $C = \gamma T + A T^3$. The values of heat capacity calculated from $\gamma$ and $\theta_D(0)$ deviate "parabolically" from the selected values, with −0.2 and +2.2 percent at the ends of the temperature range of measurements and −1.4 percent at the "trough" of the deviation.

Ramanathan and Srinivasan [92] reported measurements between 1.3 and 4.2 °K on a sample of 99.97 percent purity. The values of $\gamma$ and $\theta_D(0)$ reported are also typical of values published on gold using the two-term equation to represent the data. The 1955L $^4$He scale [111] was used. The calculated heat capacity deviate "parabolically" from the selected values, with +0.5 and 2.0 percent at the ends of the temperature range of measurements and −0.2 percent at the "trough" of the deviation.

Budworth, Hoare, and Preston [17] reported measurements from 1.8 to 4.2 °K on a material that was described as spectroscopically standardized in which individual impurities were of the order of 2 to 3 ppm. Cooling of the sample was achieved by condensing helium in a small chamber attached to the sample vessel and subsequently removing the helium by pumping. A carbon-resistance thermometer calibrated on the 1955L $^4$He scale [111] was used. The reported values of $\gamma$ and $\theta_D(0)$ based on the equation: $C = \gamma T + A T^3$ are the highest of the published values. The values of heat capacity calculated from $\gamma$ and $\theta_D(0)$ deviate "parabolically" with +2.0 and −0.6 percent at the ends of the temperature range of measurements and −1.2 percent at the "trough" of the deviation.

DuChatenier and DeNobel [34] and DuChatenier, DeNobel, and Boerstoel [36] have reported measurements between 1 and 30 °K on an annealed polycrystalline sample of 99.9999 percent purity. The analysis is stated, however, to be 2 ppm Na and less than 1 ppm Ag and Cu. No transition metals were detected. The temperatures, measured by means of a carbon-resistance thermometer, were based on the 1958 $^4$He scale [14] and the hydrogen vapor pressure work of Hoge and Arnold [59]. Helium exchange gas was used in cooling. The values of $\gamma$ and $\theta_D(0)$ reported are typical of those values published on gold. The smoothed values of heat capacity that were reported [36] exhibit an almost "sinusoidal" deviation from the selected values with a maximum of about ±3 percent. This same type of deviation has been found with their data on copper and silver [34, 35].

Crane [29] reported measurements from 1.2 to 5 °K on "pure gold" but gave no numerical values. Zimmerman and Crane [117] reported measurements on a polycrystalline sample of 99.999+ percent purity and on a single crystal of 99.99+ percent purity. The values of $\theta_D(0)$ reported for the two specimens are essentially the same, but the $\gamma$ value for the single crystal is 3 to 4 percent higher than that of the polycrystalline sample. They fitted their data to the two-term equation. The values of heat capacity calculated from the $\gamma$ and $\theta_D(0)$ reported for the polycrystalline sample deviate "parabolically" with −0.7 and +2.0 percent at the ends of the temperature range of measurement and −0.8 at the "trough" of the deviation. For the single crystal sample the corresponding deviations are +0.5, +1.9, and 0 percent.

Martin [77, 78] reported measurements in the ranges 0.4 to 1.5 °K and 3 to 30 °K on an annealed sample of 99.9999 percent purity. The measurements between 0.4 and 1.5 °K were made in a calorimeter in which the sample was cooled by means of a superconducting Pb-wire heat switch. A carbon-resistance thermometer calibrated on the 1962 $^3$He scale [104] was used. In the range 3 to 30 °K another calorimeter was used in which the cooling was achieved by circulation of helium gas between the heat sink and calorimeter. A ger-

manium thermometer was used that had been calibrated on the 1958 $^4$He scale [15], with the vapor pressure of hydrogen [116], a gas thermometer [44], and the NBS 1955 provisional scale [60, 46]. Values of $\gamma$ and $\theta_D(0)$ obtained from the measurements between 0.4 and 1.5 °K are the lowest of those published. The data reported by Martin [77, 78] were included in the selection of the best values. The values of heat capacity of Martin [77, 78] in general fall well within ±0.1 percent of the selected values.

Isaacs [61] reported measurements from 1.5 to 4.2 °K on a sample of 99.9999+ percent purity. A mechanical heat switch was used in cooling the sample. A carbon-resistance thermometer calibrated on the 1958 $^4$He scale [14] was used. Isaacs [61] showed that his data can be represented better by an equation of the form: $C = \gamma T + AT^3 + BT^5$, the coefficient for the $T^5$ term was found to be negative ($B = -0.00048 \pm 0.00025$ mJ °K$^{-6}$ mol$^{-1}$). Isaacs [101] subsequently recalculated the observations and obtained somewhat different results for $\theta_D(0)$ and essentially the same $\gamma$. The coefficient of the $T^5$ term was again found to be negative ($B = -0.0016$ ± 0.0003 mJ °K$^{-6}$ mol$^{-1}$). The values of heat capacity based on the new coefficients are in better agreement with the final selected values, the deviations of the values of heat capacity calculated using the new values of $\gamma$, $\theta_D(0)$, and $B$ range from 0 to $-1.3$ percent and those using the old values range from $-0.2$ to $+2.1$ percent.

Will and Green [115] reported measurements from 2 to 4 °K on an annealed polycrystalline sample of 99.9999 percent purity. A mechanical heat switch was used in cooling. (See the section on copper for a description of the unique adiabatic method used [24, 52, 53, 54, 115].) The values of $\gamma$ and $\theta_D(0)$ reported are among the lower group of values published on gold. Will and Green [115] used the heat-capacity equation of the form $C = \gamma T + AT^3 + BT^5$ to fit their data, the coefficient of the $T^5$ term being found to be negative ($B = -0.00108 \pm 0.00007$ mJ °K$^{-6}$ mol$^{-1}$) similar to that reported by Isaacs [61, 101]. Will and Green [115] found Martin's results [78] to fit the three-term equation. The values of heat capacity calculated using the $\gamma$, $\theta_D(0)$, and $B$ reported deviate from the selected values about $+0.1$ to $+0.6$ percent.

TABLE 5. *Sources of heat-capacity data on gold used in the analysis*

| Year | Temperature range of heat measurements °K | Purity of specimen Weight % | Electronic coefficient, $\gamma$ mJ °K$^{-2}$ mol$^{-1}$ × 10$^3$ | Debye $\theta$ at 0 °K °K | Entropy at 298.15 °K J °K$^{-1}$ mol$^{-1}$ | cal °K$^{-1}$ mol$^{-1}$ | Experimental method Calorimeter design | Thermometer | Temperature scale | Cooling of sample | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1928 | 15–212 | fine gold | | | | | VI–I [e] | Pb [e] | Pb, PRT,[e] gas, vp-H$_2$, vp-O$_2$ | gas [e] | [25] |
| 1952 | 16–309 | 99.99 (single crystal) | | | 47.30 ±0.08 [b] | 11.30 ±0.02 [b] | VI–I | Au-Ag | TC, vp-H$_2$, vp-O$_2$, vp-N$_2$, gas | gas | [48] |
| 1955 | 1–5 | 99.99+ (annealed) | 743 ±14 [a] | 164.57 ±0.14 [a] | | | VI–I | C | 1948W $^4$He | gas | [28] |
| 1959 | 1.3–4.2 | 99.97 | 764 ±29 [a] | 164.2 ±0.5 [a] | | | VI–I | C | 1948 $^4$He | MHS | [92] |
| 1960 | 1.8–4.2 | spectroscopically standardized | 870 ±26 [a] | 166.6 ±1.0 [a] | | | VI–I | C | 1955L $^4$He | cond | [17] |
| 1962 | 1–30 | 99.9999 | 740 | 165.2 | | | VI–I | C | 1958 $^4$He, vp-$^4$H$_2$ | gas | [34, 36] |
| 1962 | 1.2–5 | "pure" | (No numerical data are given in the paper) | | | | VI–I | C | vp-$^4$He | MHS | [29] |
| 1962 | 1.5–4.2 | 99.999+ | 740 ±10 [a] | 164.0 ±1.0 [a] | | | VI–I | C | 1958 $^4$He | MHS | [117] |
| 1962 | 1.5–4.2 | 99.99+ (single crystal) | 767 ±13 [a] | 164.2 ±1.2 [a] | | | VI–I | C | 1958 $^4$He | gas | [117] |
| 1963 | 12–273 | 99.99 | | 165 | 47.57 ±0.13 [b] | 11.37 ±0.03 [b] | VI–I | Pb | Pb, vp-H$_2$, vp-O$_2$, gas, Pt | gas | [45] |
| 1964 | 0.4–1.5 | 99.9999 (annealed) | 728 ±18 [a] | 162.4 ±2.0 [a] | | | VI–I | C | 1962 $^3$He | SHS | [77, 78] |
| 1964 | 3–30 | 99.9999 (annealed) | | | | | VA–C | Ge | 1958 $^4$He, vp-H$_2$, gas, NBS–1955 | cond | [77, 78] |
| 1965 | 1.5–4.2 | 99.9999+ | 729 ±18 [a,c,d] | 162.8 ±1.5 [b,c,d] | | | VI–I | C | 1958 $^4$He | MHS | [61, 62] |
| 1966 | 2–4 | 99.9999 | 730 ±7 [a,c] | 162.5 ±0.4 [a,c] | | | VA–I | C | 1958 $^4$He | MHS | [115] |

[a] These figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the precision of the values given.
[b] These figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the estimated uncertainties in the values given.
[c] From the equation of the form: $C = \gamma T + AT^3 + BT^5$, where $A = 12\pi^4 R/5[\theta_D(0)]^3$.
[d] Isaacs [62] recalculated the experimental observations and found slightly different values: $\gamma = 0.731 \pm 0.020$ mJ °K$^{-2}$ mol$^{-1}$; $\theta_D(0) = 162.4 \pm 0.6$ °K; $B = -0.0016 \pm 0.0003$ mJ °K$^{-6}$ mol$^{-1}$.
[e] See section 2 for definitions of symbols and abbreviations used.
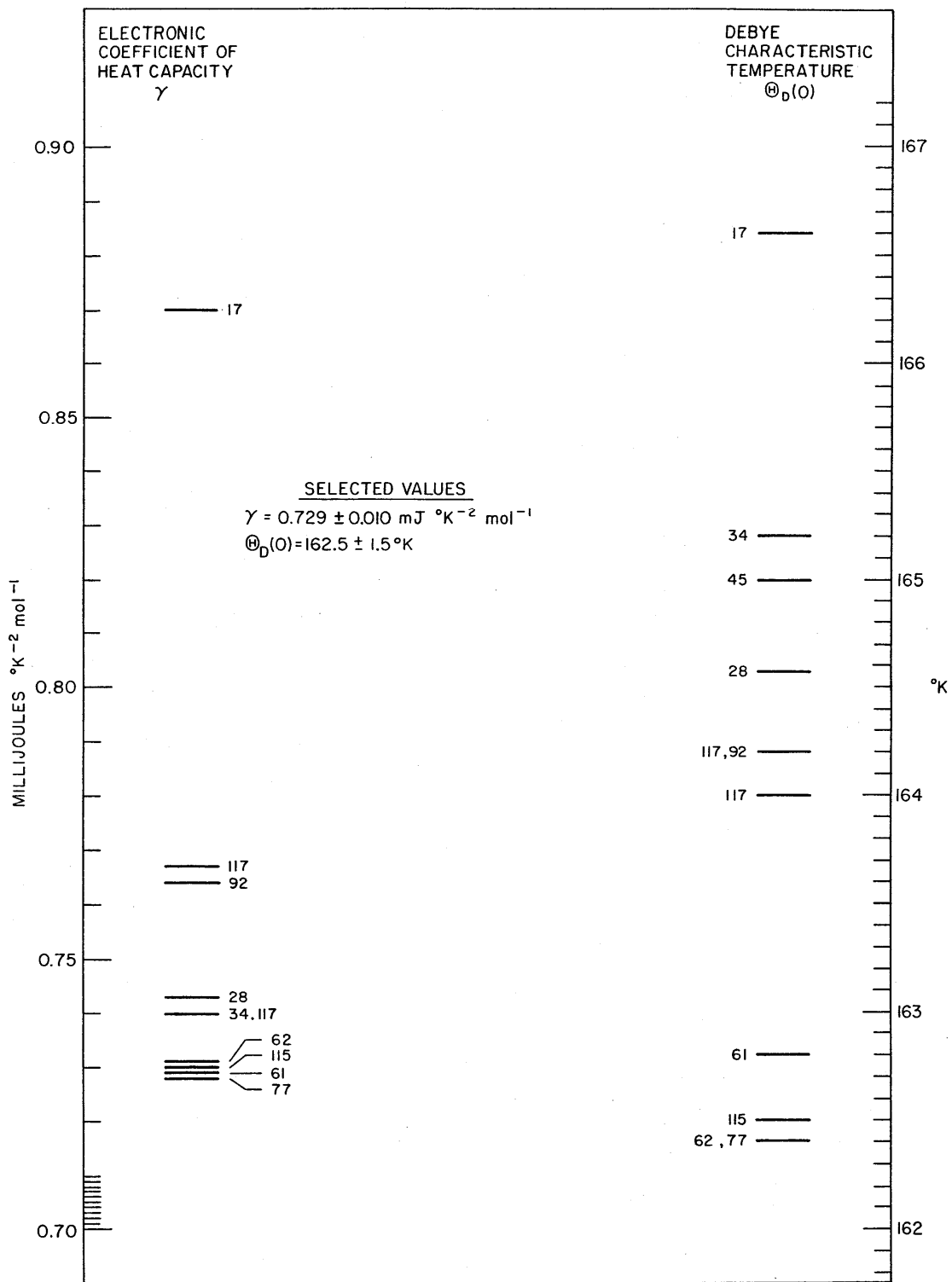
FIGURE 5. *Comparison of the reported values of electronic coefficients of heat capacity, γ, and Debye characteristic temperatures, θ_D(0), of gold.*

34
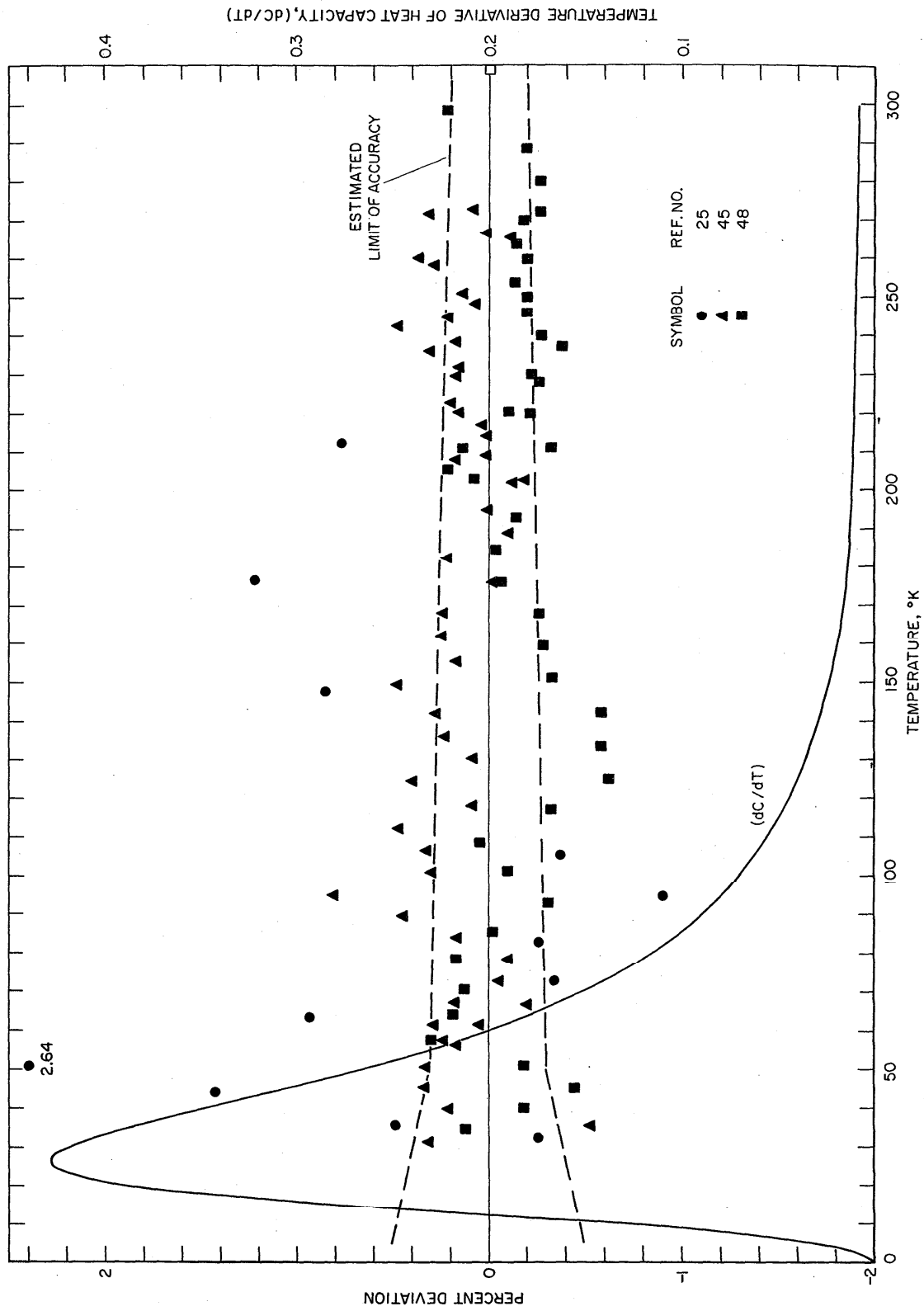
FIGURE 6a.  Deviations of the heat-capacity data of the literature on gold from the selected values in the range 30 to 300 °K.
The estimated limit of accuracy and the temperature derivative, dC/dT, in J °K⁻² mol⁻¹ of the selected values.

35

FIGURE 6b. *Deviations of the heat-capacity data of the literature on gold from the selected values in the range 0 to 30 °K and the estimated limit of accuracy of the selected values.*

36
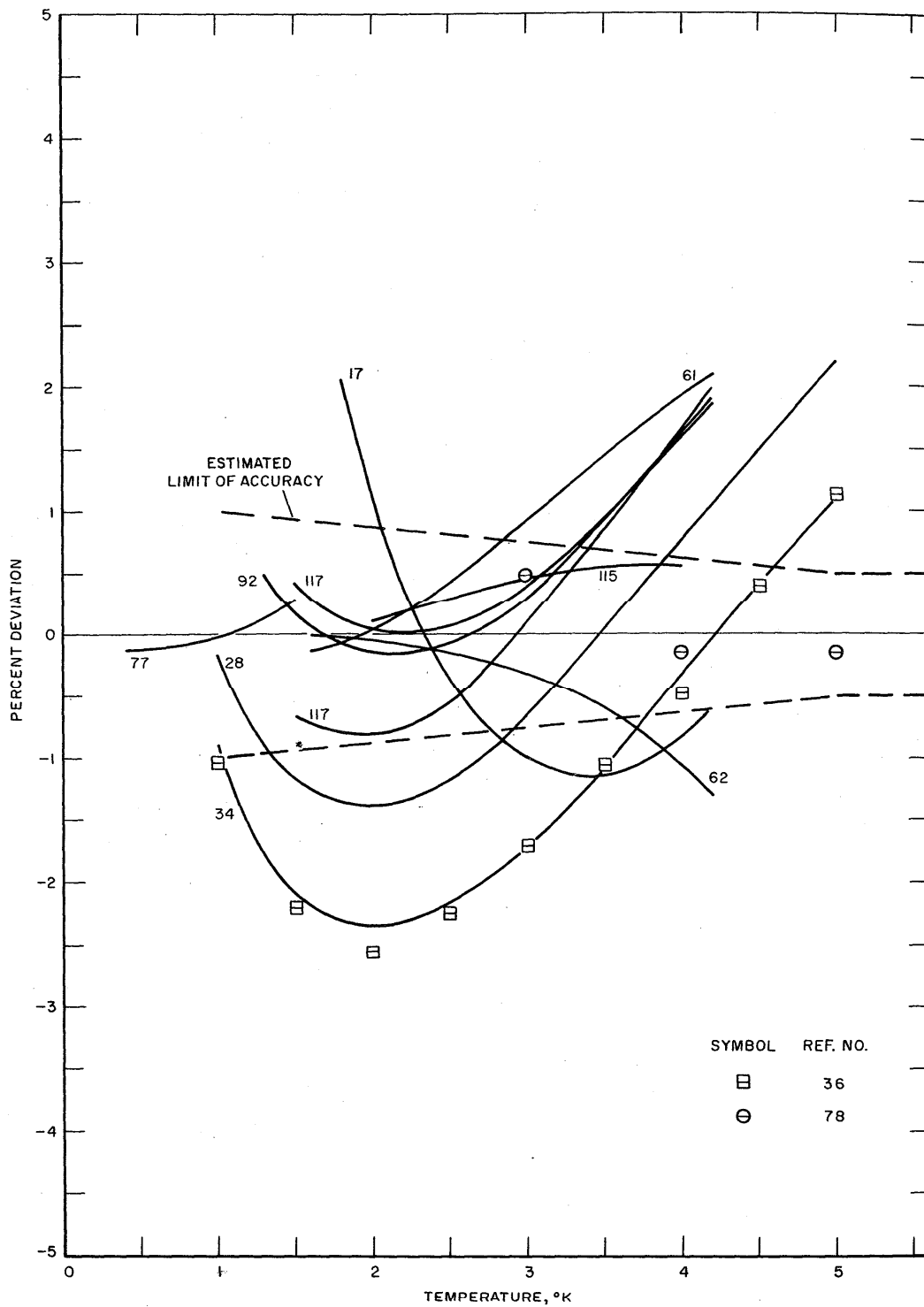
FIGURE 6c. *Deviations of the heat-capacity data of the literature on gold from the selected values in the range 0 to 5 °K and the estimated limit of accuracy of the selected values.*

37

## TABLE 6. *Thermodynamic Functions for Gold*

Gram atomic wt.= 196.9670, $T$ °K=273.15+$t$ °C, 1 cal=4.1840$J$

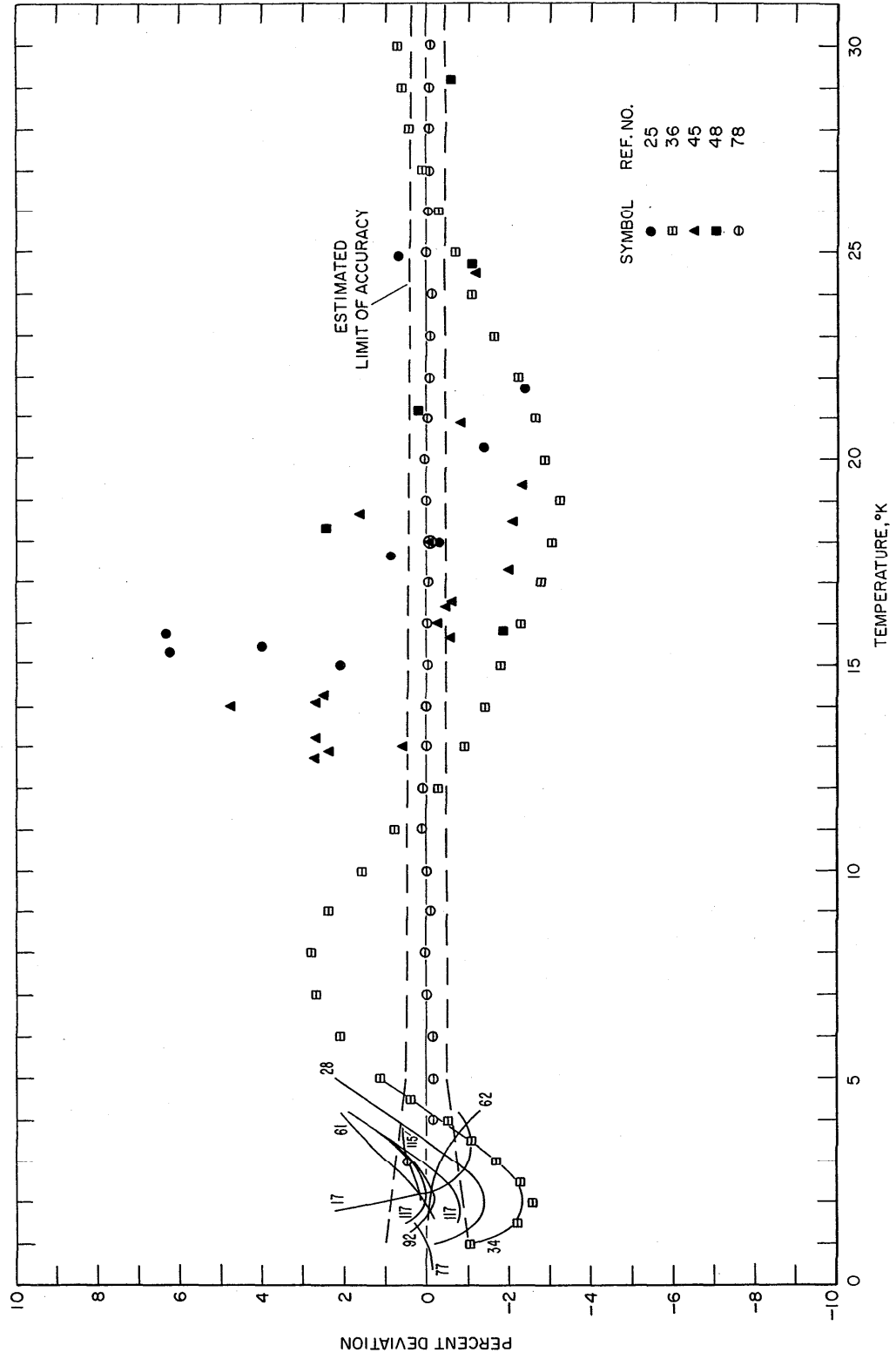| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | J/deg-mol | J/mol | J/deg-mol | J/deg-mol | J/mol | J/deg-mol |
| 1.00 | 0.00118 | 0.000478 | 0.000478 | 0.000880 | 0.000402 | 0.000402 |
| 2.00 | 0.00504 | 0.00326 | 0.00163 | 0.00266 | 0.00206 | 0.00103 |
| 3.00 | 0.0141 | 0.0123 | 0.00410 | 0.00620 | 0.00631 | 0.00210 |
| 4.00 | 0.0306 | 0.0340 | 0.00849 | 0.0123 | 0.0153 | 0.00383 |
| 5.00 | 0.0570 | 0.0768 | 0.0154 | 0.0218 | 0.0321 | 0.00641 |
| 6.00 | 0.0955 | 0.152 | 0.0253 | 0.0354 | 0.0603 | 0.0100 |
| 7.00 | 0.149 | 0.273 | 0.0390 | 0.0539 | 0.104 | 0.0149 |
| 8.00 | 0.220 | 0.456 | 0.0570 | 0.0782 | 0.170 | 0.0212 |
| 9.00 | 0.313 | 0.720 | 0.0800 | 0.109 | 0.263 | 0.0292 |
| 10.00 | 0.431 | 1.090 | 0.109 | 0.148 | 0.391 | 0.0391 |
| 11.00 | 0.577 | 1.592 | 0.145 | 0.196 | 0.562 | 0.0511 |
| 12.00 | 0.755 | 2.255 | 0.188 | 0.253 | 0.786 | 0.0655 |
| 13.00 | 0.963 | 3.112 | 0.239 | 0.322 | 1.073 | 0.0825 |
| 14.00 | 1.203 | 4.193 | 0.299 | 0.402 | 1.434 | 0.102 |
| 15.00 | 1.474 | 5.529 | 0.369 | 0.494 | 1.880 | 0.125 |
| 16.00 | 1.772 | 7.149 | 0.447 | 0.598 | 2.426 | 0.152 |
| 17.00 | 2.096 | 9.081 | 0.534 | 0.715 | 3.081 | 0.181 |
| 18.00 | 2.442 | 11.35 | 0.630 | 0.845 | 3.861 | 0.214 |
| 19.00 | 2.807 | 13.97 | 0.735 | 0.987 | 4.775 | 0.251 |
| 20.00 | 3.187 | 16.97 | 0.848 | 1.140 | 5.838 | 0.292 |
| 25.00 | 5.245 | 37.97 | 1.519 | 2.069 | 13.76 | 0.550 |
| 30.00 | 7.375 | 69.53 | 2.318 | 3.214 | 26.89 | 0.896 |
| 35.00 | 9.395 | 111.5 | 3.186 | 4.505 | 46.14 | 1.318 |
| 40.00 | 11.22 | 163.2 | 4.079 | 5.881 | 72.08 | 1.802 |
| 45.00 | 12.86 | 223.4 | 4.965 | 7.299 | 105.0 | 2.334 |
| 50.00 | 14.29 | 291.4 | 5.828 | 8.729 | 145.1 | 2.902 |
| 55.00 | 15.52 | 366.0 | 6.654 | 10.15 | 192.3 | 3.496 |
| 60.00 | 16.59 | 446.3 | 7.438 | 11.55 | 246.5 | 4.109 |
| 65.00 | 17.51 | 531.6 | 8.179 | 12.91 | 307.7 | 4.734 |
| 70.00 | 18.31 | 621.2 | 8.874 | 14.24 | 375.6 | 5.366 |
| 75.00 | 19.01 | 714.6 | 9.528 | 15.53 | 450.0 | 6.001 |
| 80.00 | 19.63 | 811.2 | 10.14 | 16.78 | 530.8 | 6.635 |
| 85.00 | 20.17 | 910.7 | 10.71 | 17.98 | 617.7 | 7.267 |
| 90.00 | 20.64 | 1013. | 11.25 | 19.15 | 710.6 | 7.895 |
| 95.00 | 21.06 | 1117. | 11.76 | 20.28 | 809.1 | 8.517 |
| 100.00 | 21.44 | 1223. | 12.23 | 21.37 | 913.3 | 9.133 |
| 105.00 | 21.77 | 1331. | 12.68 | 22.42 | 1023. | 9.740 |
| 110.00 | 22.06 | 1441. | 13.10 | 23.44 | 1137. | 10.34 |
| 115.00 | 22.33 | 1552. | 13.49 | 24.43 | 1257. | 10.93 |
| 120.00 | 22.56 | 1664. | 13.87 | 25.38 | 1382. | 11.51 |
| 125.00 | 22.78 | 1777. | 14.22 | 26.31 | 1511. | 12.09 |
| 130.00 | 22.97 | 1892. | 14.55 | 27.20 | 1645. | 12.65 |
| 135.00 | 23.15 | 2007. | 14.87 | 28.07 | 1783. | 13.21 |
| 140.00 | 23.31 | 2123. | 15.17 | 28.92 | 1925. | 13.75 |
| 145.00 | 23.45 | 2240. | 15.45 | 29.74 | 2072. | 14.29 |
| 150.00 | 23.59 | 2358. | 15.72 | 30.54 | 2223. | 14.82 |
| 155.00 | 23.70 | 2476. | 15.97 | 31.31 | 2377. | 15.34 |
| 160.00 | 23.81 | 2595. | 16.22 | 32.07 | 2536. | 15.85 |
| 165.00 | 23.91 | 2714. | 16.45 | 32.80 | 2698. | 16.35 |
| 170.00 | 24.00 | 2834. | 16.67 | 33.52 | 2864. | 16.85 |

TABLE 6. *Thermodynamic Functions for Gold*—Continued

Gram atomic wt.= 196.9670, $T$ °K=273.15+$t$ °C, 1 cal=4.1840$J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | J/deg-mol | J/mol | J/deg-mol | J/deg-mol | J/mol | J/deg-mol |
| 175.00 | 24.08 | 2954. | 16.88 | 34.21 | 3033. | 17.33 |
| 180.00 | 24.15 | 3075. | 17.08 | 34.89 | 3206. | 17.81 |
| 185.00 | 24.22 | 3196. | 17.27 | 35.55 | 3382. | 18.28 |
| 190.00 | 24.29 | 3317. | 17.46 | 36.20 | 3561. | 18.74 |
| 195.00 | 24.35 | 3438. | 17.63 | 36.83 | 3744. | 19.20 |
| 200.00 | 24.41 | 3560. | 17.80 | 37.45 | 3930. | 19.65 |
| 205.00 | 24.48 | 3683. | 17.96 | 38.05 | 4118. | 20.09 |
| 210.00 | 24.54 | 3805. | 18.12 | 38.64 | 4310. | 20.52 |
| 215.00 | 24.60 | 3928. | 18.27 | 39.22 | 4505. | 20.95 |
| 220.00 | 24.65 | 4051. | 18.41 | 39.79 | 4702. | 21.37 |
| 225.00 | 24.71 | 4174. | 18.55 | 40.34 | 4903. | 21.79 |
| 230.00 | 24.76 | 4298. | 18.69 | 40.89 | 5106. | 22.20 |
| 235.00 | 24.82 | 4422. | 18.82 | 41.42 | 5312. | 22.60 |
| 240.00 | 24.87 | 4546. | 18.94 | 41.94 | 5520. | 23.00 |
| 245.00 | 24.92 | 4671. | 19.06 | 42.46 | 5731. | 23.39 |
| 250.00 | 24.97 | 4796. | 19.18 | 42.96 | 5945. | 23.78 |
| 255.00 | 25.02 | 4921. | 19.30 | 43.46 | 6161. | 24.16 |
| 260.00 | 25.07 | 5046. | 19.41 | 43.94 | 6379. | 24.53 |
| 265.00 | 25.12 | 5171. | 19.51 | 44.42 | 6600. | 24.91 |
| 270.00 | 25.17 | 5297. | 19.62 | 44.89 | 6823. | 25.27 |
| 273.15 | 25.20 | 5376. | 19.68 | 45.18 | 6965. | 25.50 |
| 275.00 | 25.21 | 5423. | 19.72 | 45.35 | 7049. | 25.63 |
| 280.00 | 25.26 | 5549. | 19.82 | 45.81 | 7277. | 25.99 |
| 285.00 | 25.31 | 5676. | 19.91 | 46.25 | 7507. | 26.34 |
| 290.00 | 25.35 | 5802. | 20.01 | 46.69 | 7739. | 26.69 |
| 295.00 | 25.39 | 5929. | 20.10 | 47.13 | 7974. | 27.03 |
| 298.15 | 25.42 | 6009. | 20.15 | 47.40 | 8123. | 27.24 |
| 300.00 | 25.43 | 6056. | 20.19 | 47.56 | 8211. | 27.37 |

$H_0^\circ$ is the enthalpy of the solid at 0 °K and 1 atm pressure.
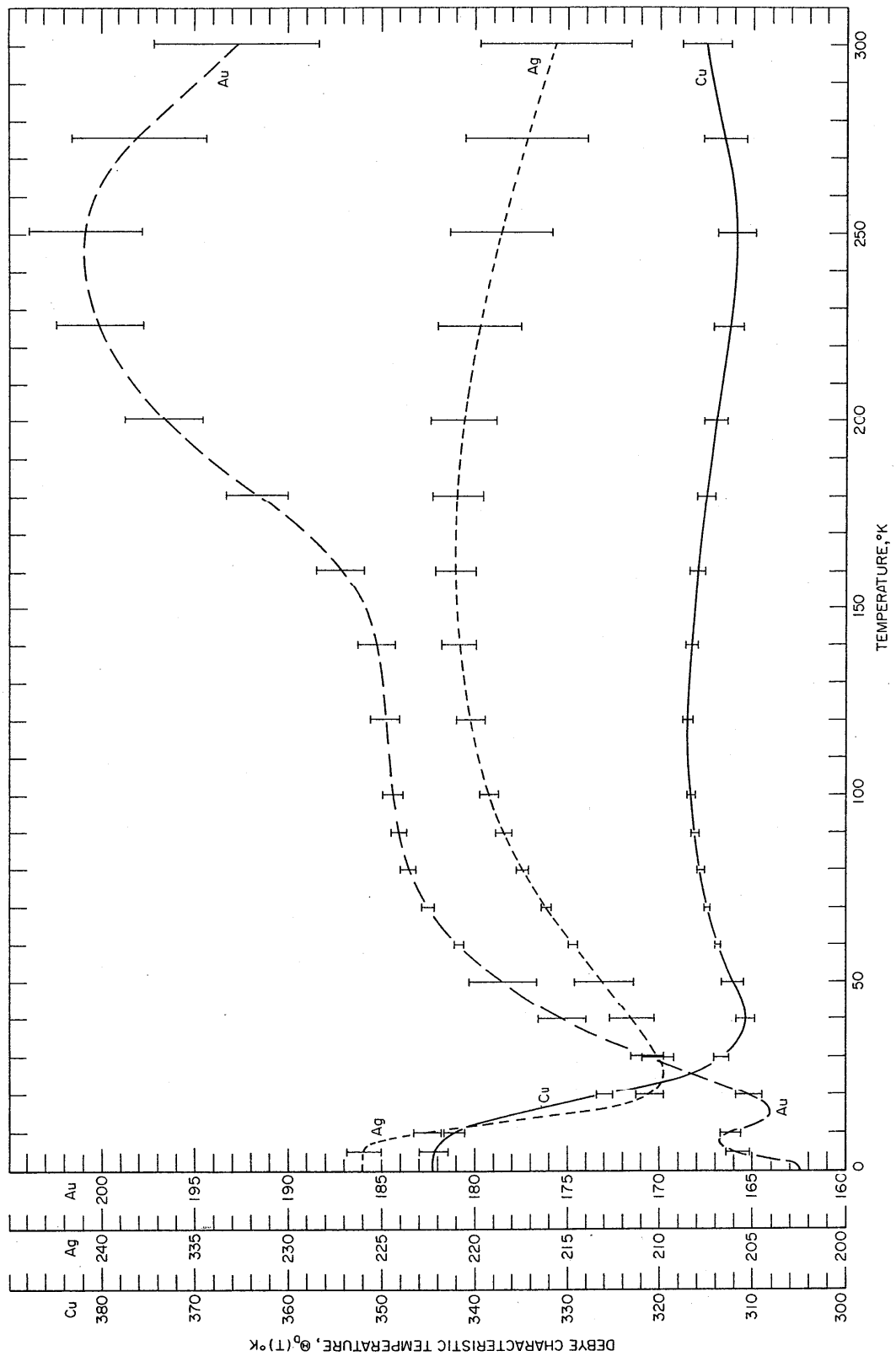
FIGURE 7. *Comparison of the Debye characteristic temperatures,* $\theta_D(T)$, *of the selected values of heat capacity of copper, silver, and gold in the range 0 to 300 °K. The values of* $\theta_D(T)$ *were calculated from the relations* $C_v = C_p - \gamma T - AC_p^2 T$ *and* $D(\theta/T) = C_v/3R$. *(See the text for further details.)* *The vertical lines at 60 °K and above correspond to 0.1 percent of the heat capacity and those below 60 °K 1 percent of the heat capacity.*

40

# 5. References

[1] Ahlers, G., Some Properties of Solid Hydrogen at Small Molar Volumes, Thesis—UCRL-10757, 133 pp. (1963), U.S. Atomic Energy Comm. Contract No. W-7405-eng-48, University of California, Lawrence Radiation Laboratory, Berkeley, Calif.

[2] Ahlers, G., Lattice heat capacity of solid hydrogen, J. Chem. Phys. **41**, 86–94 (1964).

[3] Ahlers, G., Heat capacity of copper, Rev. Sci. Instr. **37**, 477–480 (1966).

[4] Ahlers, G., The heat capacity of silver below 26 °K, J. Phys. Chem. Solids **28**, 525–527 (1967).

[5] Aoyama, S., and Kanda, E., Specific heats of nickel and cobalt at low temperature, Nippon Kagaku Zasshi **62**, 312–315 (1941).

[6] Barber, C. R., The establishment of a practical scale of temperature for the range 10–90 °K, Brit. J. Appl. Phys. **13**, 235–241 (1962).

[7] Barber, C. R., and Hayes, J. G., The derivation of the provisional reference table CCT 64, T = f(W) for platinum resistance thermometers for the range from 12 to 273.15 °K. Part II. The derivation of the table for the range from 90 to 273.15 °K, Metrologia **2**, 11–13 (1966).

[8] Barber, C. R., and Horsford, A., Differences between the thermodynamic scale and the International Practical Scale of Temperature from 0 °C to −183 °C, Metrologia **1**, 75–80 (1965).

[9] Berman, R., and Swenson, C. A., Absolute temperature scale between 4.2° and 5.2 °K, Phys. Rev. **95**, 311–314 (1954).

[10] Blakemore, J. S., Schultz, J. W., and Myers, J. G., Measurements on gallium-doped germanium thermometers, Rev. Sci. Instr. **33**, 545–551 (1962).

[11] Bleaney, B., and Hull, R. A., The determination of the vapour-pressure curve of liquid helium below 1.6 °K using a magnetic thermometer, Proc. Roy. Soc. (London) **178A**, 74–85 (1941).

[12] Bleaney, B., and Simon, F., The vapour pressure curve of liquid helium below the λ-point, Trans. Faraday Soc. **35**, 1205–1214 (1939).

[13] Borovick-Ramanov, A. S., Strelkov, P. G., Orlova, M. P., and Astrov, D. N., "The I.M.P.R. Temperature Scale from the 10 to 90 °K Region" in American Institute of Physics, Temperature, Its Measurement and Control in Science and Industry **3**, Pt. 1, pp. 113–128 (Reinhold Publishing Corp., New York, 1962).

[14] Brickwedde, F. G., van Dijk, H., Durieux, M., Clement, J. R., and Logan, J. K., The "1958 He⁴ Scale of Temperatures," J. Res. NBS **64A** (Phys. and Chem.), No. 1, 1–17 (1960).

[15] Bronson, H. L., Chisholm, H. M., and Dockerty, S. M., On the specific heats of tungsten, molybdenum, and copper, Can. J. Res. **8**, 282–303 (1933).

[16] Bronson, H. L., and Wilson, A. J. C., The heat capacities of silver, nickel, zinc, cadmium and lead from −80° to 120 °C, Can. J. Res. **14A**, 181–193 (1936).

[17] Budworth, D. W., Hoare, F. E., and Preston, J., The thermal and magnetic properties of some transition element alloys, Proc. Roy. Soc. (London) **257A**, 250–262 (1960).

[18] Burk, D. L., Estermann, I., and Friedberg, S. A., The low temperature specific heats of titanium, zirconium, and hafnium, Z. Physik. Chem. (Frankfurt) **16**, 183–193 (1958).

[19] Busey, R. H., The heat capacity of rhenium heptoxide from 15 to 300 °K. Entropy and free energy, J. Am. Chem. Soc. **78**, 3263–3266 (1956).

[20] Cameron, A. E., and Wichers, E., Report of the International Commission on Atomic Weights (1961), J. Am. Chem. Soc. **84**, 4175–4197 (1962).

[21] Cataland, G., and Plumb, H., Isotherms determined by the National Bureau of Standards acoustical thermometer in the liquid helium temperature range, J. Res. NBS **69A** (Phys. and Chem.), No. 6, 531–534 (1965).

[22] Clement, J. R., Logan, J. K., and Gaffney, J., Liquid helium vapor pressure equation, Phys. Rev. **100**, 743–744 (1955).

[23] Clement, J. R., Logan, J. K., and Gaffney, J., Une equation pour la pression de la vapeur saturée de l'hélium liquide, Proc. Conf. de Phys. des Basses Temp., Paris, 2–8 Sept. 1955, 601–604 (Suppl. Bull. Inst. Intern. Froid Paris, Annexe 1955–3).

[24] Clune, L. C., and Green, B. A., Jr., Low-temperature specific heats of α-CuSn and α-CuZn alloys, Phys. Rev. **144**, 525–528 (1966).

[25] Clusius, K., and Harteck, P., Über die spezifischen Wärmen einiger fester Körper bei tiefen Temperaturen, Z. Physik. Chem. (Leipzig) **134**, 243–263 (1928).

[26] Clusius, K., and Vaughen, J. V., Zur Temperaturmessung unterhalb von 80° absolut mittels des Bleithermometers, Z. Ges. Kalte-Ind. **36**, 215–221 (1929).

[27] Cole, A. G., Hutchens, J. O., Robie, R. A., and Stout, J. W., Apparatus and methods for low temperature heat capacity measurements. The heat capacity of standard benzoic acid, J. Am. Chem. Soc. **82**, 4807–4813 (1960).

[28] Corak, W. S., Garfunkel, M. P., Satterthwaite, C. B., and Wexler, A., Atomic heats of copper, silver, and gold from 1 °K to 5 °K, Phys. Rev. **98**, 1699–1707 (1955).

[29] Crane, L. T., Specific heats of dilute Au-Co alloys between 1.2° and 5 °K, Phys. Rev. **125**, 1902–1904 (1962).

[30] Crane, L. T., and Zimmerman, J. E., Specific heats of dilute Cu-Co alloys between 1.5 degrees and 4.5 degrees K, Phys. Rev. **123**, 113–116 (1961).

[31] Dixon, M., Hoare, F. E., Holden, T. M., and Moody, D. E., The low temperature specific heats of some pure metals (Cu, Ag, Pt, Al, Ni, Fe, Co), Proc. Roy. Soc. (London) **285A**, 561–580 (1965).

[32] Dockerty, S. M., On the specific heat of copper from −78° to 0 °C, Can. J. Res. **9**, 84–93 (1933).

[33] Dockerty, S. M., The specific heat of copper from 30° to 200 °K, Can. J. Res. **15A**, 59–66 (1937).

[34] DuChatenier, F. J., and DeNobel, J., Heat capacities of some dilute alloys, Physica **28**, 181–183 (1962).

[35] DuChatenier, F. J., and DeNobel, J., Heat capacities of pure copper and silver and of dilute alloys of Cu, Ag, Zn, Mg and Al with transition metals of the first row at low temperatures, Physica **32**, 1097–1109 (1966).

[36] DuChatenier, F. J., DeNobel, J., and Boerstoel, B. M., Specific heats of gold and dilute alloys of manganese, chromium, iron and vanadium in gold at low temperatures, Physica **32**, 561–570 (1966).

[37] Edlow, M. H., and Plumb, H. H., Reproducibility of germanium resistance thermometers at 4.2 °K, J. Res. NBS **70C** (Engr. and Instr.), No. 4, 245–254 (1966).

[38] Erickson, R. A., and Roberts, L. D., The measurement and the calculation of the liquid helium vapor pressure-temperature scale from 1° to 4.2 °K, Phys. Rev. **93**, 957–962 (1954).

[39] Estermann, I., Friedberg, S. A., and Goldman, J. E., The specific heats of several metals between 1.8° and 4.2 °K, Phys. Rev. **87**, 582–588 (1952).

[40] Eucken, A., Clusius, K., and Woitinek, H., Die Bildung einiger Metallhalogenide, insbesondere des Bromsilbers vom Standpunkt des Nernst'schen Wärmesatzes, Z. Anorg. Allgem. Chem. **203**, 39–56 (1931).

[41] Eucken, A., and Werth, H., Die spezifische Wärme einiger Metalle und Metallegierungen bei tiefen Temperaturen, Z. Anorg. Allgem. Chem. **188**, 152–172 (1930).

[42] Filby, J. D., and Martin, D. L., The electronic specific heat of silver, Can. J. Phys. **40**, 791–794 (1962).

[43] Franck, J. P., Manchester, F. D., and Martin, D. L., The specific heat of pure copper and of some dilute copper + iron alloys showing a minimum in the electrical resistance at low temperatures, Proc. Roy. Soc. (London) **263A**, 494–507 (1961).

[44] Franck, J. P., and Martin, D. L., The superconducting transition temperature of lead, Can. J. Phys. **39**, 1320–1329 (1961).

[45] Franzosini, P., and Clusius, K., Ergebnisse der Tieftemperaturforschung. XLI. Atomwärme und Entropie des Goldes zwischen 12 °K und 273 °K, Z. Naturforsch. **18a**, 1243–1246 (1963).

41

[46] Furukawa, G. T., Douglas, T. B., McCoskey, R. E., and Ginnings, D. C., Thermal properties of aluminum oxide from 0° to 1,200 °K, J. Res. NBS 57, 67–82 (1956) RP2694.

[47] Furukawa, G. T., and Reilly, M. L., Application of precise heat-capacity data to the analysis of the temperature intervals of the NBS (1955) and the International Practical Temperature Scales in the region of 90 °K, J. Res. NBS 69A (Phys. and Chem.), No. 1, 5–12 (1965).

[48] Geballe, T. H., and Giauque, W. F., The heat capacity and entropy of gold from 15 to 300 °K, J. Am. Chem. Soc. 74, 2368–2369 (1952).

[49] Giauque, W. F., Buffington, R. M., and Schulze, W. A., Copper-constantan thermocouples and the hydrogen thermometer compared from 15 to 283° absolute, J. Am. Chem. Soc. 49, 2343–2354 (1927).

[50] Giauque, W. F., Johnston, H. L., and Kelley, K. K., Hydrogen gas thermometer compared with the oxygen and hydrogen vapor-pressure thermometers by means of a copper-constantan thermocouple, J. Am. Chem. Soc. 49, 2367–2372 (1927).

[51] Giauque, W. F., and Meads, P. F., The heat capacities and entropies of aluminum and copper from 15 to 300 °K, J. Am. Chem. Soc. 63, 1897–1901 (1941).

[52] Green, B. A., Jr., Low-temperature specific heats of silver-zinc alloys. The effect of lattice dilation, Phys. Rev. 144, 528–533 (1966).

[53] Green, B. A., Jr., and Culbert, H. V., Low-temperature specific heats of AgSn alloys, Phys. Rev. 137, A1168–A1171 (1965).

[54] Green, B. A., Jr., and Valladares, A. A., Low-temperature specific heats of AgAu alloys, Phys. Rev. 142, 379–383 (1966).

[55] Griffel, M., Vest, R. W., and Smith, J. F., Heat capacity of calcium from 1.8 to 4.2 °K, J. Chem. Phys. 27, 1267–1269 (1957).

[56] Harper, D. R., III, Specific heat of copper in the interval 0° to 50 °C with a note on vacuum-jacketed calorimeters, Bull. Bur. Std. 11, 259–329 (1914) S231.

[57] Hoare, F. E., Matthews, J. C., and Walling, J. C., The thermal and magnetic properties of palladium-silver alloys, Proc. Roy. Soc. (London) 216A, 502–515 (1953).

[58] Hoare, F. E., and Yates, B., The low-temperature (2 to 4.2 °K) specific heats of palladium-silver alloys, Proc. Roy. Soc. (London) 240A, 42–53 (1957).

[59] Hoge, H. J., and Arnold, R. D., Vapor pressures of hydrogen, deuterium, and hydrogen deuteride and dew-point pressures of their mixtures, J. Res. NBS 47, 63–74 (1951) RP2228.

[60] Hoge, H. J., and Brickwedde, F. G., Establishment of a temperature scale for the calibration of thermometers between 14 and 83 °K, J. Res. NBS 22, 351–373 (1939) RP 1188.

[61] Isaacs, L. L., Low-temperature specific heat of gold, silver, and copper, J. Chem. Phys. 43, 307–308 (1965).

[62] Isaacs, L. L., Private communication, February 20, 1967.

[63] Isaacs, L. L., and Massalski, T. B., Low-temperature specific heats of alloys based on the noble metals, Cu, Ag, and Au: α-phase Cu-Zn alloys, Phys. Rev. 138, A134–A138 (1965).

[64] Kamerlingh Onnes, H., and Weber, S., Further experiments with liquid helium. O. On the measurement of very low temperatures. XXV. The determination of the temperatures which are obtained with liquid helium, especially in connection with measurements of the vapour-pressure of helium, Comm. Phys. Lab. Univ. Leiden No. 147b, 17–33 (1915).

[65] Keesom, P. H., and Pearlman, N., An anomaly in the low temperature atomic heat of silver, Phys. Rev. 88, 140–141 (1952).

[66] Keesom, P. H., and Pearlman, N., Anomaly in the low-temperature atomic heat of silver, Phys. Rev. 98, 548 (1955).

[67] Keesom, W. H., and Kamerlingh Onnes, H., The Specific Heat at Low Temperatures. I. Measurements on the Specific Heat of Lead between 14 and 80 °K and of Copper between 15° and 22 °K, Comm. Phys. Lab. Univ. Leiden No. 143, 1–26 (1914).

[68] Keesom, W. H., and Kamerlingh Onnes, H., The Specific at Low Temperatures. II. Measurements on the Specific Heat of Copper between 14 and 90 °K, Comm. Phys. Lab. Univ. Leiden, No. 147a, 1–13 (1915).

[69] Keesom, W. H., and Kok, J. A., Measurements of the specific heats of silver from 1.35 to 20.3 °K, Proc. Acad. Sci. Amsterdam 35, 301–306 (1932).

[70] Keesom, W. H., and Kok, J. A., On the specific heats of zinc and silver at liquid helium temperatures, Physica 1, 770–778 (1934).

[71] Kneip, G. D., Jr., Betterton, J. O., Jr., and Scarbrough, J. O., Low-temperature specific heats of titanium, zirconium, and hafnium, Phys. Rev. 130, 1687–1692 (1963).

[72] Kok, J. A., and Keesom, W. H., Measurements of the atomic heats of platinum and of copper from 1.2 to 20 °K, Physica 3, 1035–1045 (1936).

[73] Kunzler, J. E., Geballe, T. H., and Hull, G. W., Jr., "Germanium Resistance Thermometers" in American Institute of Physics, Temperature, Its Measurement and Control in Science and Industry 3, Pt. 1, 391–397 (Reinhold Publishing Corp., New York, 1962).

[74] Maier, C. G., and Anderson, C. T., The disposition of work energy applied to crystals, J. Chem. Phys. 2, 513–527 (1934).

[75] Manchester, F. D., A cryostat for measuring specific heats between 1 and 4.2 °K using a mechanical thermal switch, Can. J. Phys. 37, 989–1001 (1959).

[76] Martin, D. L., The specific heat of copper from 20 to 300 °K, Can. J. Phys. 38, 17–24 (1960).

[77] Martin, D. L., Anomalous low-temperature specific heat of gold, Phys. Rev. Letters 12, 723–724 (1964).

[78] Martin, D. L., Specific heats of copper, silver, and gold below 30 °K, Phys. Rev. 141, 576–582 (1966).

[79] Massalski, T. B., and Isaacs, L. L., Low-temperature specific heats of alloys based on the noble metals, Cu, Ag, and Au: α-phase Ag-Sn alloys, Phys. Rev. 138, A139–A143 (1965).

[80] McCullough, J. P., and Messerly, J. F., The Chemical Thermodynamic Properties of Hydrocarbons and Related Substances. The Use of n-Heptane as a Reference Substance for Low-Temperature Calorimetry, U.S. Bur. Mines Bull. 596, 15 pp. (1961).

[81] Meads, P. F., Forsythe, W. R., and Giauque, W. F., The heat capacities and entropies of silver and lead from 15 to 300 °K, J. Am. Chem. Soc. 63, 1902–1905 (1941).

[82] Moessen, G. W., Aston, J. G., and Ascah, R. G., "The Pennsylvania State University Thermodynamic Temperature Scale below 90 °K and the Normal Boiling Points of Oxygen and Normal Hydrogen on the Thermodynamic Scale" in American Institute of Physics, Temperature, Its Measurement and Control in Science and Industry 3, Pt. 1, 91–102, (Reinhold Publishing Corp., New York, 1962).

[83] Moser, H., Messung der wahren spezifischen Wärme von Silver, Nickel, β-Messing, Quarzkristall und Quarzglas zwischen +50 und 700 °C nach einer verfeinerten Methode, Physik. Z. 37, 737–753 (1936).

[84] O'Neal, H. R., The Low-Temperature Heat Capacity of Tin and Indium, Thesis—UCRL–10426, 66 pp. (1963), U.S. Atomic Energy Comm. Contract No. W–7405–eng–48, University of California, Lawrence Radiation Laboratory, Berkeley, Calif.

[85] Orlova, M. P., Sharevskaya, D. I., Astrov, D. N., and Krutikova, I. G., and Barber, C. R., and Hayes, J. G., The derivation of the provisional reference table CCT 64, T = f(W) for platinum resistance thermometers for the range from 12 to 273.15 °K. Part I. The derivation of the table for the range from 12 to 95 °K, Metrologia 2, 6–10 (1966).

[86] Osborne, D. W., Flotow, H. E., and Schreiner, F., Precise low temperature calorimetry with germanium resistance thermometers, Proceedings of the 1966 Low Temperature Calorimetry Conference, Technical University of Helsinki, Otaniemi, August 26–29, 1966, Suomalaisen

Tiedeakat. Toimituksia (Ann. Acad. Sci. Fennicae) (A.VI), No. 210, 35–39 (1966).

[87] Osborne, D. W., Flotow, H. E., and Schreiner, F., Calibration and use of germanium resistance thermometers for precise heat capacity measurements from 1 to 25 °K. High purity copper for interlaboratory heat capacity comparisons, Rev. Sci. Instr. **38**, 159–168 (1967).

[88] Osborne, D. W., Westrum, E. F., Jr., and Lohr, H. R., The heat capacity and thermodynamic functions of tetrauranium nonoxide from 5 to 310 degrees K, J. Am. Chem. Soc. **79**, 529–530 (1957).

[89] Phillips, N. E., Low-temperature heat capacities of gallium, cadmium, and copper, Phys. Rev. **134**, A385–A391 (1964).

[90] Plumb, H., and Cataland, G., Acoustical thermometer and the National Bureau of Standards provisional temperature scale 2–20 (1965), Metrologia **2**, 127–139 (1966).

[91] Ramanathan, K. G., and Srinivasan, T. M., Lattice and electronic specific heats of copper and silver, J. Sci. Ind. Res. (India) **16B**, 277–279 (1957).

[92] Ramanathan, K. G., and Srinivasan, T. M., The atomic heats of gold, platinum and antimony at liquid helium temperatures, Proc. Indian Acad. Sci. **49A**, 55–60 (1959).

[93] Rayne, J. A., The heat capacity of copper below 4.2 °K, Australian J. Phys. **9**, 189–197 (1956).

[94] Rayne, J. A., Heat capacity of silver below 4.2 °K, Proc. Phys. Soc. (London) **69B**, 482–483 (1956).

[95] Roberts, T. R., Sherman, R. H., and Sydoriak, S. G., The 1962 He³ Scale of Temperatures. III. Evaluation and status, J. Res. NBS **68A** (Phys. and Chem.), No. 6, 567–578 (1964).

[96] Rorer, D. C., Onn, D. G., and Meyer, H., Thermodynamic properties of molybdenum in its superconducting and normal state, Phys. Rev. **138**, A1661–A1668 (1965).

[97] Roth, W. A., and Scheel, K., Landolt-Bornstein, Physikalisch-Chemische Tabellen, 5 Aufl. II, 1049 (J. Springer, Berlin, 1923).

[98] Royal Society Mond Laboratory, Cambridge, Great Britain, La Température dans le Domaine de l'Hélium Liquide, Annexe T–15, T151–T160, Comité Intern. des Poids et Mesures, Procès-Verbaux des Séances 1952, Deuxieme Serie, Tome XXIII–A (Gauthier-Villars, Paris, 1953).

[99] Rubin, T., Johnston, H. L., and Altman, H., The temperature scale of the Ohio State University Cryogenic Laboratory. J. Am. Chem. Soc. **73**, 3401–3404 (1951).

[100] Sandenaw, T. A., Heat Capacity of Copper Below 300 °K. A Test of Two Calorimeter Designs, LA2307, 19 pp. (1959), U.S. Atomic Energy Comm. Contract No. W–7405–eng–36, University of California, Los Alamos Scientific Laboratory, Los Alamos, N. Mex.

[101] Sargent, G. A., Isaacs, L. I., and Massalski, T. B., Low-temperature specific heats of α-phase copper-silver alloys, Phys. Rev. **143**, 420–422 (1966).

[102] Schmidt, G., and Keesom, W. H., New measurements of liquid helium temperatures. I. The boiling point of helium. Physica **4**, 963–970 (1937).

[103] Schmidt, G., and Keesom, W. H., New measurements of liquid helium temperatures. II. The vapour pressure curve of liquid helium, Physica **4**, 971–977 (1937).

[104] Sherman, R. H., Sydoriak, S. G., and Roberts, T. R., The 1962 He³ Scale of Temperatures. IV. Tables. J. Res. NBS **68A** (Phys. and Chem.), No. 6, 579–588 (1964).

[105] Shinozaki, S. S., and Arrott, A., Electronic specific heat of dilute alloys: Fe(Ti), Fe(V), Fe(Cr), Fe(Mn), Fe(Co), Fe(Ni), Fe(Al), Fe(Si), Fe(Mo), Fe(W), and Ag(Au), Phys. Rev. **152**, 611–622 (1966).

[106] Stimson, H. F., International Practical Temperature Scale of 1948. Text revision of 1960, J. Res. NBS **65A** (Phys. and Chem.), No. 3, 139–145 (1961).

[107] Sydoriak, S. G., and Roberts, T. R., Thermodynamic properties of liquid helium three. Vapor pressures below 1 °K, Phys. Rev. **106**, 175–182 (1957).

[108] Sydoriak, S. G., Roberts, T. R., and Sherman, R. H., The 1962 He³ Scale of Temperatures. II. Derivation, J. Res. NBS **68A** (Phys. and Chem.), No. 6, 559–565 (1964).

[109] Sydoriak, S. G., and Sherman, R. H., The 1962 He³ Scale of Temperatures. I. New vapor pressure comparisons, J. Res. NBS **68A** (Phys. and Chem.), No. 6, 547–558 (1964).

[110] United States National Bureau of Standards, National Applied Mathematics Laboratories, Computation Laboratory, Tables of Lagrangian Interpolation Coefficients (Columbia University Press, New York, 1944).

[111] van Dijk, H., and Durieux, The temperature scale in the liquid helium region, Proc. Conf. de Phys. des Basses Temp., Paris, 2–8 Sept. 1955, 595–600 (Suppl. Bull. Inst. Intern. Froid, Paris, Annexe, 1955–3).

[112] van Dijk, H., and Shoenberg, D., Tables of vapour pressure of liquid helium, Nature **164**, 151 (1949).

[113] Veal, B. W., and Rayne, J. A., Heat capacity of β-CuZn below 4.2 °K, Phys. Rev. **128**, 551–555 (1962).

[114] West, E. D., and Ginnings, D. C., The heat capacity of aluminum oxide in the range 300 to 700 °K, J. Phys. Chem. **61**, 1573 (1957).

[115] Will, T. A., and Green, B. A., Jr., Specific heats of Au and AuSn at low temperatures, Phys. Rev. **150**, 519–522 (1966).

[116] Woolley, H. W., Scott, R. B., and Brickwedde, F. G., Compilation of thermal properties of hydrogen in its various isotopic and ortho-para modifications, J. Res. NBS **41**, 379–475 (1948) RP1932.

[117] Zimmerman, J. E., and Crane, L. T., Anomalous lattice specific heat of gold and zinc at liquid helium temperatures, Phys. Rev. **126**, 513–516 (1962).

[118] Zimmerman, J. E., and Hoare, F. E., Low-temperature specific heat of dilute Cu-Mn alloys, J. Phys. Chem. Solids **17**, 52–56 (1960).

[119] Berge, P., and Blanc, G., Calorimètre Adiabatique, J. Phys. and Radium Phys. Appliquée **21**, Suppl. No. 7, 129A–133A (1960).

[120] Griffiths, E. H., and Griffiths, E., The capacity for heat of metals at different temperatures, being an account of experiments performed in the research laboratory of the University College of South Wales Monmouthshire, Phil. Trans. Roy. Soc. (London) **213A**, 119–185 (1913).

[121] Griffiths, E. H., and Griffiths, E., The capacity for heat of metals at different temperatures, Proc. Roy. Soc. (London) **88A**, 549–560 (1913).

[122] Griffiths, E. H., and Griffiths, E., The capacity for heat of metals at low temperatures, Phil. Trans. Roy. Soc. (London) **214A**, 319–357 (1914).

[123] Griffiths, E. H., and Griffiths, E., The capacity for heat of metals at low temperatures, Proc. Roy. Soc. (London) **90A**, 557–560 (1914).

[124] Hirano, K., Maniwa, H., and Takagi, Y., Specific-heat measurements on quench-annealed Al, Cu, and α-phase alloys of Cu, J. Phys. Soc. Japan **10**, 909–910 (1955).

[125] Honda, K., and Tokunaga, M., On the true specific heat of some metals and alloys, Sci. Rept. Tohoku Imp. Univ. (1), **23**, 816–834 (1935).

[126] Honda, K., and Tokunaga, M., On the determination of true specific heats of some metals and alloys, Kinzoku No Kenkyu **12**, 267–279 (1935).

[127] Martin, D. L., A modified continuous-heating calorimeter for the temperature range 15° to 300 °K, Can. J. Phys. **40**, 1166–1173 (1962).

[128] Martin, D. L., The specific heats of some alkali halides at very low temperatures, Proc. Phys. Soc. (London) **83**, 99–108 (1964).

[129] Mendelssohn, K., and Closs, J. O., Calorimetrische Untersuchungen im Temperaturgebiet des flüssigen Heliums, Z. Physik. Chem. (Leipzig) **19B**, 291–298 (1932).

[130] Mustajoki, A., Messungen der wahren spezifischen Wärme der KCl-KBr-Mischkristalle im Temperaturbereich 50–450 °C, Suomalaisen Tiedeakat. Toimituksia (Ann. Acad. Sci. Fennicae) (A.I), No. 98, 1–45 (1951).

[131] Pawel, R. E., and Stansbury, E. E., The specific heat of copper, nickel and copper-nickel alloys, J. Phys. Chem. Solids **26**, 607–613 (1965).

[132] Persoz, B., Nouvelles méthodes de mesure de la chaleur spécifique vraie de métaux a haute température, Ann Phys. (Paris) (II) **14**, 237–301 (1940).

43

[133] Rayne, J. A., Specific heats of metals below one degree absolute, Phys. Rev. **95**, 1428–1434 (1954).

[134] Senozan, N. M., I. Similarity Principle and Isotope Effect in Superconducting Indium. II. Low-Temperature Heat Capacity of Niobium, Thesis–UCRL–11901, 106 pp. (1965), U.S. Atomic Energy Comm. Contract No. W–7405–eng–48, University of California, Lawrence Radiation Laboratory, Berkeley, Calif.

[135] Sykes, C., Methods for investigating thermal changes occurring during transformations in a solid solution, Proc. Roy. Soc. (London) **148A**, 422–446 (1935).

[136] Thomas, W. J., and Davies, R. M., The determination of specific heats by an eddy current method. Part II. Experimental, Phil. Mag. (7) **24**, 713–744 (1937).

## APPENDIX 1. *Thermodynamic Functions for Copper*

Gram atomic wt.=63.5400, $T$ °K=273.15+$t$ °C, 1 cal=4.1840 $J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | Cal/deg-mol | Cal/mol | Cal/deg-mol | Cal/deg-mol | Cal/mol | Cal/deg-mol |
| 1.00 | 0.000177 | 0.000086 | 0.000086 | 0.000258 | 0.000165 | 0.000165 |
| 2.00 | 0.000423 | 0.000378 | 0.000189 | 0.000451 | 0.000516 | 0.000258 |
| 3.00 | 0.000805 | 0.000978 | 0.000326 | 0.000689 | 0.00108 | 0.000360 |
| 4.00 | 0.00139 | 0.00206 | 0.000514 | 0.000995 | 0.00192 | 0.000479 |
| 5.00 | 0.00225 | 0.00385 | 0.000771 | 0.00139 | 0.00310 | 0.000620 |
| 6.00 | 0.00346 | 0.00668 | 0.00111 | 0.00190 | 0.00474 | 0.000790 |
| 7.00 | 0.00508 | 0.0109 | 0.00156 | 0.00255 | 0.00695 | 0.000994 |
| 8.00 | 0.00720 | 0.0170 | 0.00213 | 0.00336 | 0.00990 | 0.00124 |
| 9.00 | 0.00990 | 0.0255 | 0.00283 | 0.00436 | 0.0137 | 0.00153 |
| 10.00 | 0.0133 | 0.0370 | 0.00370 | 0.00557 | 0.0187 | 0.00187 |
| 11.00 | 0.0174 | 0.0523 | 0.00475 | 0.00702 | 0.0250 | 0.00227 |
| 12.00 | 0.0224 | 0.0721 | 0.00601 | 0.00874 | 0.0328 | 0.00274 |
| 13.00 | 0.0284 | 0.0974 | 0.00749 | 0.0108 | 0.0426 | 0.00327 |
| 14.00 | 0.0355 | 0.129 | 0.00923 | 0.0131 | 0.0545 | 0.00389 |
| 15.00 | 0.0439 | 0.169 | 0.0113 | 0.0159 | 0.0689 | 0.00459 |
| 16.00 | 0.0538 | 0.218 | 0.0136 | 0.0190 | 0.0863 | 0.00539 |
| 17.00 | 0.0651 | 0.277 | 0.0163 | 0.0226 | 0.107 | 0.00630 |
| 18.00 | 0.0783 | 0.348 | 0.0194 | 0.0267 | 0.132 | 0.00731 |
| 19.00 | 0.0933 | 0.434 | 0.0228 | 0.0313 | 0.161 | 0.00845 |
| 20.00 | 0.110 | 0.536 | 0.0268 | 0.0365 | 0.194 | 0.00972 |
| 25.00 | 0.230 | 1.363 | 0.0545 | 0.0729 | 0.460 | 0.0184 |
| 30.00 | 0.405 | 2.928 | 0.0976 | 0.130 | 0.958 | 0.0319 |
| 35.00 | 0.631 | 5.496 | 0.157 | 0.208 | 1.792 | 0.0512 |
| 40.00 | 0.894 | 9.296 | 0.232 | 0.309 | 3.077 | 0.0769 |
| 45.00 | 1.178 | 14.47 | 0.322 | 0.431 | 4.920 | 0.109 |
| 50.00 | 1.471 | 21.09 | 0.422 | 0.570 | 7.415 | 0.148 |
| 55.00 | 1.765 | 29.18 | 0.531 | 0.724 | 10.65 | 0.194 |
| 60.00 | 2.054 | 38.73 | 0.646 | 0.890 | 14.68 | 0.245 |
| 65.00 | 2.332 | 49.70 | 0.765 | 1.066 | 19.56 | 0.301 |
| 70.00 | 2.596 | 62.03 | 0.886 | 1.248 | 25.34 | 0.362 |
| 75.00 | 2.843 | 75.63 | 1.008 | 1.436 | 32.05 | 0.427 |
| 80.00 | 3.072 | 90.43 | 1.130 | 1.627 | 39.71 | 0.496 |
| 85.00 | 3.285 | 106.3 | 1.251 | 1.819 | 48.32 | 0.568 |
| 90.00 | 3.480 | 123.2 | 1.369 | 2.013 | 57.90 | 0.643 |
| 95.00 | 3.660 | 141.1 | 1.485 | 2.206 | 68.45 | 0.721 |
| 100.00 | 3.825 | 159.8 | 1.598 | 2.398 | 79.96 | 0.800 |
| 105.00 | 3.977 | 179.3 | 1.708 | 2.588 | 92.43 | 0.880 |
| 110.00 | 4.116 | 199.6 | 1.814 | 2.776 | 105.8 | 0.962 |
| 115.00 | 4.244 | 220.5 | 1.917 | 2.962 | 120.2 | 1.045 |
| 120.00 | 4.362 | 242.0 | 2.017 | 3.145 | 135.5 | 1.129 |
| 125.00 | 4.470 | 264.1 | 2.113 | 3.326 | 151.6 | 1.213 |
| 130.00 | 4.571 | 286.7 | 2.205 | 3.503 | 168.7 | 1.298 |
| 135.00 | 4.663 | 309.8 | 2.295 | 3.677 | 186.7 | 1.383 |
| 140.00 | 4.749 | 333.3 | 2.381 | 3.848 | 205.5 | 1.468 |
| 145.00 | 4.828 | 357.2 | 2.464 | 4.016 | 225.1 | 1.553 |

Gram atomic wt.=63.5400, $T$ °K=273.15+$t$ °C, 1 cal=4.1840 $J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | Cal/deg-mol | Cal/mol | Cal/deg-mol | Cal/deg-mol | Cal/mol | Cal/deg-mol |
| 150.00 | 4.901 | 381.6 | 2.544 | 4.181 | 245.6 | 1.638 |
| 155.00 | 4.969 | 406.3 | 2.621 | 4.343 | 266.9 | 1.722 |
| 160.00 | 5.032 | 431.3 | 2.695 | 4.502 | 289.1 | 1.807 |
| 165.00 | 5.090 | 456.6 | 2.767 | 4.658 | 312.0 | 1.891 |
| 170.00 | 5.145 | 482.2 | 2.836 | 4.811 | 335.6 | 1.974 |
| 175.00 | 5.196 | 508.0 | 2.903 | 4.960 | 360.1 | 2.058 |
| 180.00 | 5.244 | 534.1 | 2.967 | 5.107 | 385.2 | 2.140 |
| 185.00 | 5.289 | 560.4 | 3.029 | 5.252 | 411.1 | 2.222 |
| 190.00 | 5.331 | 587.0 | 3.089 | 5.393 | 437.7 | 2.304 |
| 195.00 | 5.371 | 613.8 | 3.147 | 5.532 | 465.1 | 2.385 |
| 200.00 | 5.408 | 640.7 | 3.203 | 5.669 | 493.1 | 2.465 |
| 205.00 | 5.443 | 667.8 | 3.258 | 5.803 | 521.7 | 2.545 |
| 210.00 | 5.476 | 695.1 | 3.310 | 5.934 | 551.1 | 2.624 |
| 215.00 | 5.507 | 722.6 | 3.361 | 6.064 | 581.1 | 2.703 |
| 220.00 | 5.537 | 750.2 | 3.410 | 6.191 | 611.7 | 2.781 |
| 225.00 | 5.565 | 778.0 | 3.458 | 6.315 | 643.0 | 2.858 |
| 230.00 | 5.591 | 805.8 | 3.504 | 6.438 | 674.9 | 2.934 |
| 235.00 | 5.616 | 833.9 | 3.548 | 6.558 | 707.4 | 3.010 |
| 240.00 | 5.640 | 862.0 | 3.592 | 6.677 | 740.5 | 3.085 |
| 245.00 | 5.663 | 890.3 | 3.634 | 6.793 | 774.1 | 3.160 |
| 250.00 | 5.684 | 918.6 | 3.675 | 6.908 | 808.4 | 3.234 |
| 255.00 | 5.704 | 947.1 | 3.714 | 7.021 | 843.2 | 3.307 |
| 260.00 | 5.722 | 975.7 | 3.753 | 7.132 | 878.6 | 3.379 |
| 265.00 | 5.740 | 1004. | 3.790 | 7.241 | 914.5 | 3.451 |
| 270.00 | 5.757 | 1033. | 3.826 | 7.348 | 951.0 | 3.522 |
| 273.15 | 5.767 | 1051. | 3.848 | 7.415 | 974.2 | 3.567 |
| 275.00 | 5.773 | 1062. | 3.861 | 7.454 | 988.0 | 3.593 |
| 280.00 | 5.788 | 1091. | 3.896 | 7.558 | 1026. | 3.663 |
| 285.00 | 5.803 | 1120. | 3.929 | 7.661 | 1064. | 3.732 |
| 290.00 | 5.818 | 1149. | 3.961 | 7.762 | 1102. | 3.800 |
| 295.00 | 5.832 | 1178. | 3.993 | 7.862 | 1141. | 3.868 |
| 298.15 | 5.840 | 1196. | 4.013 | 7.923 | 1166. | 3.911 |
| 300.00 | 5.845 | 1207. | 4.024 | 7.960 | 1181. | 3.936 |

$H_0^\circ$ is the enthalpy of the solid at 0 °K and 1 atm pressure.

APPENDIX 2. *Thermodynamic Functions for Silver*

Gram atomic wt.$=107.8700$, $T \, ^\circ K = 273.15 + t \, ^\circ C$, 1 cal$=4.1840 J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| $^\circ K$ | Cal/deg-mol | Cal/mol | Cal/deg-mol | Cal/deg-mol | Cal/mol | Cal/deg-mol |
| 1.00 | 0.000196 | 0.000088 | 0.000088 | 0.000251 | 0.000156 | 0.000156 |
| 2.00 | 0.000633 | 0.000472 | 0.000236 | 0.000500 | 0.000522 | 0.000261 |
| 3.00 | 0.00155 | 0.00151 | 0.000505 | 0.000911 | 0.00121 | 0.000404 |
| 4.00 | 0.00320 | 0.00382 | 0.000955 | 0.00156 | 0.00242 | 0.000606 |
| 5.00 | 0.00581 | 0.00823 | 0.00165 | 0.00254 | 0.00444 | 0.000889 |
| 6.00 | 0.00964 | 0.0158 | 0.00264 | 0.00391 | 0.00763 | 0.00127 |
| 7.00 | 0.0150 | 0.0280 | 0.00400 | 0.00578 | 0.0124 | 0.00178 |
| 8.00 | 0.0222 | 0.0464 | 0.00580 | 0.00822 | 0.0194 | 0.00242 |
| 9.00 | 0.0316 | 0.0731 | 0.00812 | 0.0114 | 0.0291 | 0.00323 |
| 10.00 | 0.0437 | 0.110 | 0.0110 | 0.0153 | 0.0423 | 0.00423 |
| 11.00 | 0.0590 | 0.162 | 0.0147 | 0.0201 | 0.0600 | 0.00545 |
| 12.00 | 0.0778 | 0.230 | 0.0191 | 0.0260 | 0.0830 | 0.00691 |
| 13.00 | 0.101 | 0.318 | 0.0245 | 0.0331 | 0.112 | 0.00865 |
| 14.00 | 0.128 | 0.432 | 0.0309 | 0.0416 | 0.150 | 0.0107 |
| 15.00 | 0.160 | 0.576 | 0.0384 | 0.0515 | 0.196 | 0.0131 |
| 16.00 | 0.197 | 0.754 | 0.0471 | 0.0630 | 0.253 | 0.0158 |
| 17.00 | 0.240 | 0.972 | 0.0572 | 0.0762 | 0.323 | 0.0190 |
| 18.00 | 0.287 | 1.235 | 0.0686 | 0.0912 | 0.406 | 0.0226 |
| 19.00 | 0.338 | 1.547 | 0.0814 | 0.108 | 0.506 | 0.0266 |
| 20.00 | 0.394 | 1.912 | 0.0956 | 0.127 | 0.623 | 0.0311 |
| 25.00 | 0.733 | 4.689 | 0.188 | 0.249 | 1.543 | 0.0617 |
| 30.00 | 1.141 | 9.354 | 0.312 | 0.418 | 3.193 | 0.106 |
| 35.00 | 1.580 | 16.15 | 0.461 | 0.627 | 5.791 | 0.165 |
| 40.00 | 2.012 | 25.14 | 0.629 | 0.866 | 9.514 | 0.238 |
| 45.00 | 2.417 | 36.23 | 0.805 | 1.127 | 14.49 | 0.322 |
| 50.00 | 2.786 | 49.25 | 0.985 | 1.401 | 20.81 | 0.416 |
| 55.00 | 3.117 | 64.03 | 1.164 | 1.683 | 28.51 | 0.518 |
| 60.00 | 3.411 | 80.36 | 1.339 | 1.967 | 37.64 | 0.627 |
| 65.00 | 3.669 | 98.08 | 1.509 | 2.250 | 48.18 | 0.741 |
| 70.00 | 3.896 | 117.0 | 1.671 | 2.530 | 60.13 | 0.859 |
| 75.00 | 4.096 | 137.0 | 1.827 | 2.806 | 73.48 | 0.980 |
| 80.00 | 4.272 | 157.9 | 1.974 | 3.076 | 88.19 | 1.102 |
| 85.00 | 4.429 | 179.7 | 2.114 | 3.340 | 104.2 | 1.226 |
| 90.00 | 4.568 | 202.2 | 2.246 | 3.597 | 121.6 | 1.351 |
| 95.00 | 4.692 | 225.3 | 2.372 | 3.848 | 140.2 | 1.476 |
| 100.00 | 4.804 | 249.1 | 2.491 | 4.091 | 160.0 | 1.600 |
| 105.00 | 4.904 | 273.4 | 2.603 | 4.328 | 181.1 | 1.725 |
| 110.00 | 4.994 | 298.1 | 2.710 | 4.558 | 203.3 | 1.848 |
| 115.00 | 5.075 | 323.3 | 2.811 | 4.782 | 226.7 | 1.971 |
| 120.00 | 5.148 | 348.8 | 2.907 | 5.000 | 251.1 | 2.093 |
| 125.00 | 5.215 | 374.7 | 2.998 | 5.211 | 276.7 | 2.213 |
| 130.00 | 5.276 | 401.0 | 3.084 | 5.417 | 303.2 | 2.332 |
| 135.00 | 5.331 | 427.5 | 3.167 | 5.617 | 330.8 | 2.450 |
| 140.00 | 5.382 | 454.3 | 3.245 | 5.812 | 359.4 | 2.567 |
| 145.00 | 5.429 | 481.3 | 3.319 | 6.002 | 388.9 | 2.682 |
| 150.00 | 5.473 | 508.6 | 3.390 | 6.186 | 419.4 | 2.796 |
| 155.00 | 5.513 | 536.0 | 3.458 | 6.367 | 450.8 | 2.908 |
| 160.00 | 5.550 | 563.7 | 3.523 | 6.542 | 483.1 | 3.019 |
| 165.00 | 5.585 | 591.5 | 3.585 | 6.713 | 516.2 | 3.128 |
| 170.00 | 5.617 | 619.5 | 3.644 | 6.881 | 550.2 | 3.236 |

Gram atomic wt.= 107.8700, $T$ °K=273-15+$t$ °C, 1 cal=4.1840 $J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | Cal/deg-mol | Cal/mol | Cal/deg-mol | Cal/deg-mol | Cal/mol | Cal/deg-mol |
| 175.00 | 5.647 | 647.7 | 3.701 | 7.044 | 585.0 | 3.343 |
| 180.00 | 5.676 | 676.0 | 3.756 | 7.203 | 620.6 | 3.448 |
| 185.00 | 5.702 | 704.5 | 3.808 | 7.359 | 657.0 | 3.551 |
| 190.00 | 5.727 | 733.0 | 3.858 | 7.512 | 694.2 | 3.654 |
| 195.00 | 5.751 | 761.7 | 3.906 | 7.661 | 732.1 | 3.755 |
| 200.00 | 5.773 | 790.5 | 3.953 | 7.807 | 770.8 | 3.854 |
| 205.00 | 5.795 | 819.5 | 3.997 | 7.949 | 810.2 | 3.952 |
| 210.00 | 5.815 | 848.5 | 4.040 | 8.089 | 850.3 | 4.049 |
| 215.00 | 5.834 | 877.6 | 4.082 | 8.226 | 891.1 | 4.145 |
| 220.00 | 5.852 | 906.8 | 4.122 | 8.361 | 932.5 | 4.239 |
| 225.00 | 5.870 | 936.1 | 4.161 | 8.492 | 974.7 | 4.332 |
| 230.00 | 5.886 | 965.5 | 4.198 | 8.622 | 1017. | 4.424 |
| 235.00 | 5.902 | 995.0 | 4.234 | 8.748 | 1061. | 4.514 |
| 240.00 | 5.917 | 1025. | 4.269 | 8.873 | 1105. | 4.604 |
| 245.00 | 5.932 | 1054. | 4.303 | 8.995 | 1150. | 4.692 |
| 250.00 | 5.946 | 1084. | 4.335 | 9.115 | 1195. | 4.780 |
| 255.00 | 5.959 | 1114. | 4.367 | 9.233 | 1241. | 4.866 |
| 260.00 | 5.973 | 1143. | 4.398 | 9.349 | 1287. | 4.951 |
| 265.00 | 5.985 | 1173. | 4.428 | 9.463 | 1334. | 5.035 |
| 270.00 | 5.997 | 1203. | 4.457 | 9.575 | 1382. | 5.118 |
| 273.15 | 6.005 | 1222. | 4.474 | 9.644 | 1412. | 5.170 |
| 275.00 | 6.009 | 1233. | 4.485 | 9.685 | 1430. | 5.200 |
| 280.00 | 6.020 | 1263. | 4.512 | 9.793 | 1479. | 5.281 |
| 285.00 | 6.032 | 1294. | 4.539 | 9.900 | 1528. | 5.361 |
| 290.00 | 6.042 | 1324. | 4.564 | 10.00 | 1578. | 5.440 |
| 295.00 | 6.053 | 1354. | 4.590 | 10.11 | 1628. | 5.519 |
| 298.15 | 6.059 | 1373. | 4.605 | 10.17 | 1660. | 5.567 |
| 300.00 | 6.063 | 1384. | 4.614 | 10.21 | 1679. | 5.596 |

$H_0^\circ$ is the enthalpy of the solid at 0 °K and 1 atm pressure.

## APPENDIX 3. *Thermodynamic Functions for Gold*

Gram atomic wt.=196.9670, $T$ °K=273.15+$t$ °C, 1 cal=4.1840 $J$.

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | Cal/deg-mol | Cal/mol | Cal/deg-mol | Cal/deg-mol | Cal/mol | Cal/deg-mol |
| 1.00 | 0.000282 | 0.000114 | 0.000114 | 0.000303 | 0.000181 | 0.000181 |
| 2.00 | 0.00121 | 0.000779 | 0.000390 | 0.000728 | 0.000669 | 0.000335 |
| 3.00 | 0.00337 | 0.00294 | 0.000980 | 0.00158 | 0.00178 | 0.000593 |
| 4.00 | 0.00732 | 0.00811 | 0.00203 | 0.00304 | 0.00402 | 0.00101 |
| 5.00 | 0.0136 | 0.0184 | 0.00367 | 0.00530 | 0.00812 | 0.00162 |
| 6.00 | 0.0228 | 0.0363 | 0.00605 | 0.00854 | 0.0149 | 0.00249 |
| 7.00 | 0.0356 | 0.0652 | 0.00931 | 0.0130 | 0.0256 | 0.00366 |
| 8.00 | 0.0526 | 0.109 | 0.0136 | 0.0188 | 0.0414 | 0.00517 |
| 9.00 | 0.0748 | 0.172 | 0.0191 | 0.0262 | 0.0637 | 0.00708 |
| 10.00 | 0.103 | 0.261 | 0.0261 | 0.0355 | 0.0944 | 0.00944 |
| 11.00 | 0.138 | 0.380 | 0.0346 | 0.0469 | 0.135 | 0.0123 |
| 12.00 | 0.180 | 0.539 | 0.0449 | 0.0607 | 0.189 | 0.0157 |
| 13.00 | 0.230 | 0.744 | 0.0572 | 0.0770 | 0.258 | 0.0198 |
| 14.00 | 0.288 | 1.002 | 0.0716 | 0.0961 | 0.344 | 0.0246 |
| 15.00 | 0.352 | 1.321 | 0.0881 | 0.118 | 0.451 | 0.0301 |
| 16.00 | 0.424 | 1.709 | 0.107 | 0.143 | 0.581 | 0.0363 |
| 17.00 | 0.501 | 2.170 | 0.128 | 0.171 | 0.738 | 0.0434 |
| 18.00 | 0.584 | 2.712 | 0.151 | 0.202 | 0.924 | 0.0514 |
| 19.00 | 0.671 | 3.339 | 0.176 | 0.236 | 1.143 | 0.0602 |
| 20.00 | 0.762 | 4.055 | 0.203 | 0.273 | 1.397 | 0.0699 |
| 25.00 | 1.254 | 9.074 | 0.363 | 0.495 | 3.290 | 0.132 |
| 30.00 | 1.763 | 16.62 | 0.554 | 0.768 | 6.429 | 0.214 |
| 35.00 | 2.246 | 26.66 | 0.762 | 1.077 | 11.03 | 0.315 |
| 40.00 | 2.682 | 38.99 | 0.975 | 1.406 | 17.23 | 0.431 |
| 45.00 | 3.073 | 53.40 | 1.187 | 1.745 | 25.10 | 0.558 |
| 50.00 | 3.415 | 69.64 | 1.393 | 2.086 | 34.68 | 0.694 |
| 55.00 | 3.709 | 87.47 | 1.590 | 2.426 | 45.96 | 0.836 |
| 60.00 | 3.964 | 106.7 | 1.778 | 2.760 | 58.93 | 0.982 |
| 65.00 | 4.185 | 127.1 | 1.955 | 3.086 | 73.55 | 1.132 |
| 70.00 | 4.377 | 148.5 | 2.121 | 3.404 | 89.78 | 1.283 |
| 75.00 | 4.544 | 170.8 | 2.277 | 3.711 | 107.6 | 1.434 |
| 80.00 | 4.691 | 193.9 | 2.424 | 4.009 | 126.9 | 1.586 |
| 85.00 | 4.820 | 217.7 | 2.561 | 4.298 | 147.6 | 1.737 |
| 90.00 | 4.934 | 242.1 | 2.689 | 4.577 | 169.8 | 1.887 |
| 95.00 | 5.034 | 267.0 | 2.810 | 4.846 | 193.4 | 2.036 |
| 100.00 | 5.123 | 292.4 | 2.924 | 5.107 | 218.3 | 2.183 |
| 105.00 | 5.202 | 318.2 | 3.030 | 5.359 | 244.5 | 2.328 |
| 110.00 | 5.273 | 344.4 | 3.131 | 5.602 | 271.9 | 2.471 |
| 115.00 | 5.336 | 370.9 | 3.225 | 5.838 | 300.5 | 2.613 |
| 120.00 | 5.393 | 397.7 | 3.314 | 6.066 | 330.2 | 2.752 |
| 125.00 | 5.444 | 424.8 | 3.399 | 6.288 | 361.1 | 2.889 |
| 130.00 | 5.490 | 452.2 | 3.478 | 6.502 | 393.1 | 3.024 |
| 135.00 | 5.533 | 479.7 | 3.554 | 6.710 | 426.1 | 3.156 |
| 140.00 | 5.571 | 507.5 | 3.625 | 6.912 | 460.2 | 3.287 |
| 145.00 | 5.606 | 535.4 | 3.693 | 7.108 | 495.2 | 3.415 |
| 150.00 | 5.637 | 563.5 | 3.757 | 7.299 | 531.2 | 3.542 |
| 155.00 | 5.665 | 591.8 | 3.818 | 7.484 | 568.2 | 3.666 |
| 160.00 | 5.691 | 620.2 | 3.876 | 7.664 | 606.1 | 3.788 |
| 165.00 | 5.714 | 648.7 | 3.932 | 7.840 | 644.8 | 3.908 |
| 170.00 | 5.735 | 677.3 | 3.984 | 8.011 | 684.5 | 4.026 |

Gram atomic wt.=196.9670, $T$ °K=273.15+$t$ °C, 1 cal=4.1840 $J$

| $T$ | $C_P^\circ$ | $H_T^\circ - H_0^\circ$ | $(H_T^\circ - H_0^\circ)/T$ | $S_T^\circ$ | $-(G_T^\circ - H_0^\circ)$ | $-(G_T^\circ - H_0^\circ)/T$ |
|---|---|---|---|---|---|---|
| °K | Cal/deg-mol | Cal/mol | Cal/deg-mol | Cal/deg-mol | Cal/mol | Cal/deg-mol |
| 175.00 | 5.754 | 706.0 | 4.035 | 8.177 | 724.9 | 4.142 |
| 180.00 | 5.772 | 734.9 | 4.083 | 8.339 | 766.2 | 4.257 |
| 185.00 | 5.789 | 763.8 | 4.128 | 8.498 | 808.3 | 4.369 |
| 190.00 | 5.805 | 792.7 | 4.172 | 8.652 | 851.2 | 4.480 |
| 195.00 | 5.820 | 821.8 | 4.214 | 8.803 | 894.8 | 4.589 |
| 200.00 | 5.835 | 850.9 | 4.255 | 8.951 | 939.2 | 4.696 |
| 205.00 | 5.850 | 880.2 | 4.293 | 9.095 | 984.3 | 4.802 |
| 210.00 | 5.864 | 909.4 | 4.331 | 9.236 | 1030. | 4.906 |
| 215.00 | 5.878 | 938.8 | 4.367 | 9.374 | 1077. | 5.008 |
| 220.00 | 5.892 | 968.2 | 4.401 | 9.510 | 1124. | 5.109 |
| 225.00 | 5.906 | 997.7 | 4.434 | 9.642 | 1172. | 5.208 |
| 230.00 | 5.919 | 1027. | 4.466 | 9.772 | 1220. | 5.306 |
| 235.00 | 5.932 | 1057. | 4.497 | 9.900 | 1270. | 5.402 |
| 240.00 | 5.944 | 1087. | 4.528 | 10.02 | 1319. | 5.497 |
| 245.00 | 5.956 | 1116. | 4.557 | 10.15 | 1370. | 5.591 |
| 250.00 | 5.968 | 1146. | 4.585 | 10.27 | 1421. | 5.683 |
| 255.00 | 5.980 | 1176. | 4.612 | 10.39 | 1472. | 5.774 |
| 260.00 | 5.992 | 1206. | 4.638 | 10.50 | 1525. | 5.864 |
| 265.00 | 6.004 | 1236. | 4.664 | 10.62 | 1577. | 5.953 |
| 270.00 | 6.015 | 1266. | 4.689 | 10.73 | 1631. | 6.040 |
| 273.15 | 6.022 | 1285. | 4.704 | 10.80 | 1665. | 6.095 |
| 275.00 | 6.026 | 1296. | 4.713 | 10.84 | 1685. | 6.126 |
| 280.00 | 6.037 | 1326. | 4.737 | 10.95 | 1739. | 6.211 |
| 285.00 | 6.048 | 1356. | 4.760 | 11.06 | 1794. | 6.296 |
| 290.00 | 6.059 | 1387. | 4.782 | 11.16 | 1850. | 6.378 |
| 295.00 | 6.069 | 1417. | 4.804 | 11.26 | 1906. | 6.460 |
| 298.15 | 6.075 | 1436. | 4.817 | 11.33 | 1941. | 6.511 |
| 300.00 | 6.079 | 1447. | 4.825 | 11.37 | 1962. | 6.541 |

$H_0^\circ$ is the enthalpy of the solid at 0 °K and 1 atm pressure.