Critical Analysis of Heat—Capacity Data and Evaluation of Thermodynamic Properties of Ruthenium, Rhodium, Palladium, Iridium, and Platinum from 0 to 300K. A Survey of the Literature Data on Osmium.

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George T. Furukawa, Martin L. Reilly, and John S. Gallagher



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# Critical Analysis of Heat-Capacity Data and Evaluation of Thermodynamic Properties of Ruthenium, Rhodium, Palladium, Iridium, and Platinum from 0 to 300 K. A Survey of the Literature Data on Osmium

#### George T. Furukawa, Martin L. Reilly, and John S. Gallagher

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The literature sources of heat-capacity data on ruthenium, rhodium, palladium, osmium, iridium, and platinum have been compiled and the data critically analyzed. Except for osmium where data arc lacking, best values of thermodynamic properties have been evaluated between 0 and 300 K from the analyses. The literature values of heat capacity, the electronic coefficient of heat capacity  $(\hat{y})$ , and the zero K limiting Debye characteristic temperature (0,0)) are compared. The sources of 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.

Key words: Calorimetry; critically evaluated data; Debye temperature ( $\theta$ ); electronic coefficient of heat capacity ( $\gamma$ ); enthalpy; entropy; Gibbs energy; heat capacity; iridium; osmium; palladium; platinum: rhodium; ruthenium; thermodynamic properties.

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#### 1. Introduction

This publication on the noble-metal transition elements is the second in a series of reviews sponsored by the Office of Standard Reference Data, presenting critical analysis of heat-capacity data in the literature. The objective of this phase of work is to select "best" estimates for the values of the heat capacity over the temperature range 0 to 300 K, and to present tables of thermodynamic functions derived from these values. The information has broad application in science and technology, particularly in the study of chemical equilibria for which accurate derived thermodynamic properties are needed and in the study of the solid state (lattice dynamics, electronic distributions, energy states of magnetic materials, order-disorder processes, and critical phenomena) for which reliable heat-capacity data provide a powerful tool in the development and testing of the theories of fundamental properties of matter. Another important purpose of the critical review is to indicate substances and temperature ranges where the experimental data are inadequate or non-existent and thereby stimulate the research to fill the gaps.

A comprehensive exposition of the scope of this series of publications was given in the first monograph  $[29]^{1}$ ; consequently only a brief restatement is given here.

1. The intent of this work is to locate, examine, and report all sources of original experimental measurements of heat capacity or relative enthalpy in the temperature range 0 to 300 K which are available in the open literature. In addition, all known measurements above 300 K are reviewed and are included in the analysis, if they are useful in establishing the heat capacity in the region of 300 K.

2. With the exception of the relative enthalpy data above 300 K, the sources of data used in the analysis

are discussed in the chronological order of the journal publication date. Whenever the authors reported revisions or new measurements, the new data have been considered chronologically with the original work. A chronological list of the data sources including brief descriptions of the experimental procedure is tabulated for each substance.

3. The best values of heat capacity are estimated from the literature values. An intercomparison between the literature data and the selected values is presented as a deviation plot. The estimated limit of accuracy of the selected values is shown in the same plot. The curve for the first temperature derivative of the selected heat capacities,  $(dC_p/dT)$ , and the curve of the Debye characteristic temperature,  $\theta_D(T)$ , are plotted against temperature (see section 3.1 for the description of the method employed to obtain  $\theta_D(T)$ ). The curves for  $dC_p/dT$  and  $\theta_D(T)$  show the smoothness and the "shape" of the selected values of heat capacity. The value of  $\theta_D(T)$  is the base for the final selected value of heat capacity (see section 3).

4. The search of the literature is as current and complete as practical.<sup>2</sup> Limited data or results incidental to measurements on other substances may be overlooked because of a lack of reference to the data or an inappropriate title not descriptive of the work. The authors gratefully acknowledge the cooperation and contributions of Y. S. Touloukian of the Thermophysical Properties Research Center, Purdue University, Lafayette, Indiana; V. J. Johnson of the Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado; and T. F. Connolly of the Research Materials Information Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, in the bibliographic search.

5. The pertinent bibliography of the literature sources that have been examined is arranged alphabetically by author with the title of the publication and journal reference at the end for each publication. References found later in the study are appended alphabetically to the first set.

6. For each element the information is arranged in the following order:

- a) discussion of data sources with statements of the degree of deviation from the selected values,
- b) table of sources of heat-capacity data analyzed,
- c) plot of  $\gamma$  and  $\theta_D(0)$  (only palladium and platinum),
- d) plots of literature data relative to the selected values,
- e) plots of  $dC_p/dT$  and  $\theta_D(T)$  as a function of T,
- f) plot of the limit of accuracy of the selected value,
- g) table of thermodynamic functions in joules,
- h) bibliography for all elements (at the end),
- i) table of thermodynamic functions in calories (in the appendix).

<sup>&</sup>lt;sup>1</sup>Figures in brackets indicate the literature references in section 5.

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<sup>&</sup>quot; This work was completed in 1970. The authors expect that most papers published prior to 1970 have been included in the analysis.

### 2. Units, Symbols, and Definitions

The International System of Units (SI) [61] is used throughout this monograph. The following units, symbols, and definitions are used.

kg = kilogram

- g = gram
- m = meter
- s = second
- K = kelvin
- $N = newton = kg \cdot m / s^2$
- $J = joule = N \cdot m$
- $\frac{\mathbf{A} = \text{``dilation coefficient'' appearing in the}}{\text{relationship}}$

$$C_v^l = C_p^l (1 - \underline{A} C_p^l T)$$

- B = temperature coefficient of nuclear heat capacity
- $C_p$  = heat capacity at constant pressure (1 atm)
- $C_p^{l}$ =lattice heat capacity at constant pressure (1 atm)

 $C_p^l = C_p - (\gamma T + \text{other non-lattice terms})$ 

- $C_v^l$  = estimated lattice heat capacity at constant volume
- H = enthalpy
- G =Gibbs energy
- Q = quantity of heat
- $R gas constant 8.3143 \text{ J/K} \cdot mol$
- S = entropy
- T =temperature, kelvin
- $\mathbf{k} = \text{coefficient of isothermal compressibility}$
- v = specific volume
- $\theta_D(0) =$  limiting Debye characteristic temperature at 0 K
- $\theta_D(T) =$  Debye temperature at T calculated from the value of  $C_{L}^{l}$  at T (see eq (7))

t = time

- $\alpha$  = temperature coefficient of linear expansion g = temperature coefficient of electronic heat capacity, mJ/K<sup>2</sup> · mol
- atm = standard atmosphere =  $101325 \text{ N/m}^2$
- cal = defined thermochemical calorie = 4.184 J
- mol = mass of a pure substance comprising as many elementary entities as there are atoms in 0.012 kg of carbon-12 [11].

The temperature scales used in the literature for the substances analyzed in this publication are uncertain to the extent that no basis could be established to convert the data to the International Practical Temperature Scale of 1968 [88]. For all practical purposes the temperature scale of the final selected values can be taken to be the prevailing temperature scale [88]. The limit of uncertainty of the values of heat capacity is considered to be greater than that of the temperature scale.

The prevailing energy unit of this publication will be the SI 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 familiar 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 [11] whenever the experimental data warranted the conversion.

In tables 1, 3, 5, 7, and 9, certain abbreviations are used to describe the experimental methods. The abbreviations are defined as follows:

#### Calorimeter Design

- VI-I = isothermal jacket vacuum calorimeter operated by incremental heating.
- VA-I = adiabatic vacuum calorimeter operated by incremental heating.
- MM = method of mixtures.
- MM-Cu = method of mixtures, receiving calorimeter constructed of copper block.
- MM-water = method of mixtures with water in the receiving calorimeter.
  - MM-ice=method of mixtures, Bunsen ice calorimeter.
  - MM-DE = method of mixtures, Bunsen ice-type calorimeter, using diphenyl ether.
    - CH = continuous heating, heat capacity being determined from the relation:

(dQ/dt)/(dT/dt).

Temperature Scale

vp = vapor pressure.

- gas = gas thermometer.
- vp-4He=helium vapor pressure scale with no official designation.
- Year-<sup>4</sup>He=helium vapor pressure scale with official designation.
- 1948.<sup>4</sup>He = He vapor pressure scale, see references [80, 94].
- 1955E-<sup>4</sup>He = modification to 1948-<sup>4</sup>He by Clement, Logan, and Gaffney [12, 13].
- 1955L-<sup>4</sup>He = modification to 1948-<sup>4</sup>He by van Dijk and Durieux [92, 93].
- 1958-<sup>4</sup>He = compromise of 1955E-<sup>4</sup>He and 1955L-<sup>4</sup>He [6].
  - Pb=scale based on a table of electrical resistance of Pb versus temperature [79, 20].

or

where

- MS = magnetic susceptibility temperature scale.
- ITS = International Temperature Scale of 1927 [8].
- IPTS-48 = International Practical Temperature Scale of 1948 [84, 85].
- IPTS-68 = International Practical Temperature Scale of 1968 [88].
- NBS-1955 = National Bureau of Standards Provisional Temperature Scale of 1955 [34, 62], based on the resistance of platinum thermometer compared with helium-gas thermometer between 10 and 90 K.
- NBS (2-20 K) = National Bureau of Standards Provisional Temperature Scale between 2 and 20 K [71], based on resistance of germanium thermometers compared with an acoustical temperature scale.
  - TC (Pt-Rh) = platinum versus platinum-rhodium alloy thermocouple [88].

### Thermometer

Resistance thermometers are indicated by solid metals, alloys, and semi-conductors: Pt, Pb, phosphorbronze, constantan, C, Ge, Eureka.

Hg = mercury in glass thermometer.

MS = magnetic susceptibility thermometer. TC (Pt-Rh) = platinum versus platinum-rhodium alloy thermocouple.

Cooling of Sample

gas = gas heat exchange with heat sink.

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

MHS = mechanical heat switch.

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

#### Selected Values

The selected values of this monograph are assigned estimated limits of uncertainty which are shown plotted for each of the elements. The uncertainty was estimated by examining (1) the scatter in the data, (2) the estimated uncertainties in the results obtained by the same laboratories on other substances, (3) the calorimetric method, and (4) the purity of the sample. The error in the selected values is estimated to have a fifty percent chance of being no larger than the uncertainty figure.

### 3. Method of Analysis of the Heat-Capacity Data

The literature data that were examined in this analysis have been obtained by two experimental methods: heat-capacity measurements and relativeenthalpy measurements. In the case of heat-capacity measurements, except at very low temperatures, the authors generally published the observed and/or smoothed numerical values of heat-capacity. In the measurements at temperatures below about 4 K, the original numerical data were usually omitted from the paper. Published instead were plots and derived parameters of theoretical importance, in particular, the zero K Debye limiting characteristic temperature,  $\theta_D(0)$ , and the coefficient of electronic heat capacity,  $\gamma$ . A least squares approximation to the equation

$$C/T = \gamma + A|T^2, \tag{1}$$

$$C = \gamma T + AT^3, \tag{2}$$

(3)

$$\theta_D(0) = \left[\frac{5}{12\pi^4 R} A\right]^{-1/3},$$

was used by most authors as a means of estimating these parameters from the experimental data. The tolerances assigned by the authors to the parameters  $\gamma$  and  $\theta_D(0)$ , unless they were explicitly defined otherwise, were assumed to be related to statistical quantities determined in the fitting process and were, therefore, considered to be a measure of the precision rather than the accuracy of the measurements. In order to use such results in the present analysis, representative numerical heat capacity "data points" were calculated from the published parameters and the appropriate equation for the temperature range of the experimental measurements. The deviations of these values from the selected values are shown as curves in the deviation plots. Wherever numerical values were published the deviations are shown as "points".

The usual method for obtaining heat data for temperatures above about 300 K is by measurement of relative enthalpy (relative to 273 K or 298 K). The measurements are usually made over large temperature intervals and the smoothed results are presented in the form of an enthalpy equation, empirical in nature, representing the entire experimental temperature range for a given phase of the material under investigation. The equation yields satisfactory values of the enthalpy relative to that at the reference temperature of the experiment, but the heat capacities calculated from its temperature derivative are apt to be less reliable, particularly in the region of the reference temperature. When such data are used for analysis, the observed enthalpy difference is usually compared with the temperature integral of the selected heat capacities over the corresponding experimental temperature interval. Because of the lack of overlapping measurements employing the two experimental methods, the above refinement was not made in the analysis of the data on the elements discussed in this monograph. Numerical values of heat capacity were obtained using the published relative enthalpy equation up to as high as 500 K and were employed as a guide to estimate the best values of heat capacity in the region of 300 K.

Initially in the analysis, the observed solid-phase heat capacities for the elements at constant pressure,  $C_p$ , were taken to be the sum of independent terms describing the lattice heat capacity at constant pressure,  $C_p^l$ , the electronic heat capacity,  $\gamma T$ , and the nuclear heat capacity,  $B/T^2$ ,

$$C_p = C_p^l + \gamma T + B/T^2. \tag{4}$$

Further, the lattice heat capacity at constant volume,  $C_v^l$ , was assumed to be related to the constant pressure value in the manner originally proposed by Nernst and Lindemann [64].

$$C_v^l = C_p^l \ (1 - \underline{A} \ C_p^l \ T).$$
<sup>(5)</sup>

$$\underline{\mathbf{A}} = 9 \ \alpha^2 \ v/\underline{\mathbf{k}} \ (C_p^l)^2, \tag{6}$$

where

 $\alpha$  = temperature coefficient of linear expansion,

v = specific volume,

and  $\underline{\mathbf{k}} = \text{coefficient of isothermal compressibility.}$ 

This choice for the representation of the constant volume lattice heat-capacity has negligible influence on the values of  $\theta_D(T)$  at low temperatures. However, at the higher temperatures, above about 100 K, the value of  $C_v^l$ , and thus  $\theta_D(T)$ , was somewhat dependent upon the choice of <u>A</u>.

The initial value of <u>A</u> was calculated from room temperature values for  $\alpha$ , v, and <u>k</u>, taken from the literature, combined with the value of  $C_p^l$  selected at 298.15 K for this analysis. After a series of preliminary test analyses, the values of  $\theta_D(T)$  were found to take on a simpler shape if <u>A</u> were negative for the noblemetal transition elements. Instead of assigning an unusual negative value for <u>A</u>, the analysis for this monograph was made with <u>A</u>=0.

The Debye temperature,  $\theta_D(T)$ , was calculated for each data point from the constant volume lattice heat capacity, satisfying the relationship

$$C_{v}^{i}(T) = 9R \left(\frac{T}{\theta_{D}(T)}\right)^{3} \int_{0}^{y} \frac{x^{4} e^{x} dx}{(e^{x} - 1)^{2}},$$
(7)

where  $x = \theta/T$  and  $y = \theta_D(T)/T$ . This expression of the constant volume lattice heat capacity derived by

Debye [22], is based upon the assumption that the distribution of vibrational frequencies in the solid is proportional to the square of the frequency up to a limiting maximum frequency. Although no real solid conforms to the Debye model of heat capacity except at extremely low temperatures, the  $\theta_D(T)$  representation is a slowly varying function of temperature and, therefore, was convenient in analyzing the experimental data. The smooth curve of  $\theta_D(T)$  vs T, shown on the plot, was obtained from the "experimental"  $\theta_D(T)$ by numerical smoothing techniques using a digital computer. Except at the low temperatures, the values of  $\theta_D(T)$  were expected to follow a simple curve. In certain temperature regions, particularly those lacking in data or where data points were suspected of error, it was necessary to introduce estimates for the  $\theta_D(T)$ 's based upon personal judgment. (Since in the final analysis A was taken to be zero, the values of  $\theta_D(T)$ at the higher temperatures deviate slightly from a simple curve for the elements analyzed in this paper.)

The data analysis involved the following steps. The experimental data at the lowest temperatures were carefully examined to select first the best value for y. Then, values of  $C_v^l$  were calculated, employing equations (4) and (5), for all experimental data points, including those evaluated, as previously mentioned, at selected temperatures from heat-capacity equations. (For the elements considered here,  $\underline{A}$  and the temperature coefficient of nuclear heat capacity, B, were both taken to be zero.) Smoothed values of  $\theta_D(T)$  were obtained as a function of temperature by numerically smoothing the values of  $\theta_D(T)$  obtained from  $C_v^l$  (see eq (7)). "Smoothed values" of  $C_p$  were then computed as a function of temperature from the "smoothed  $\theta_D(T)$ " and the selected value of  $\gamma$ ; the values of the derivative  $dC_p/dT$  were also computed. The smoothed values of  $\theta_D(T)$  and of  $dC_p/dT$  were required to follow a simple curve; if not, the analysis was repeated either after removing the data points that were considered from the results of the fitting process to be of low accuracy or after selecting a new value of  $\gamma$ . This analytical process was repeated until values of  $\theta_D(T)$  and  $dC_p/dT$  that met the requirement were obtained. In the analysis, the data of certain investigators may be given more weight because of the greater consistency of their data with the above requirement; while the data of others, although relatively precise, may be given very little weight because of their lack of consistency with the overall requirement. Some judgment was also involved, based largely on the uncertainty of results obtained on other substances by the investigator. The deviation plots indicate the relative weight that was given to different data.

Hulm and Goodman [36] found from magnetic measurements that ruthenium and osmium become superconducting at 0.47 K and 0.71 K, respectively; Jensen, Matthias, and Andreas [50] reported that rhodium and platinum would become superconducting below 0.001 K, if at all, and palladium not at all. The data analyzed are all above these superconducting temperatures. The selected values of heat capacity given in this monograph are for the normal state. Since the entropy difference between the superconductive and normal states vanishes at the critical transition temperature, the thermodynamic properties above the critical transition temperature are independent of the superconductivity.

The selected smoothed values of heat capacities at constant volume were calculated by means of eq (7) from the smoothed values of  $\theta_D(T)$ ; then the smoothed constant pressure values were calculated by eq (5) followed by eq (4) (without the term  $B/T^2$ ). Deviation plots reflect the relation between the literature data and the final selection; deviations from the selected values of the published numerical data are plotted as points and heat capacities calculated from equations are indicated as continuous curves over the experimental temperature range. The thermodynamic functions were calculated from selected values of heat capacity by numerical integration using five-point Lagrangian integration coefficients [60]. The thermodynamic relations used were:

$$H_T^{\circ} - H_0^{\circ} = \int_{\mathcal{V}}^T C_p^{\circ} dT, \qquad (8)$$

$$S_T^{\circ} - S_0^c = \int_0^{\tau} \frac{T C_p}{T} dT, \qquad (9)$$

$$G_{T}^{\circ} - H_{0}^{c} = \int_{0}^{T} (S_{T}^{\circ} - S_{0}^{c}) dT = (H_{T}^{\circ} - H_{0}^{c} - T(S_{T}^{\circ} - S_{0}^{c})).$$
(10)

The thermodynamic functions  $(H_T^\circ - H_0^c)/T$  and  $G_T^\circ - H_0^c)/T$  were obtained from values of eq (8) and (10) by dividing by the corresponding temperature T. In the above equations  $H_0^\circ$  and  $S_0^\circ$  apply to the reference state of the solid at 0 K and 1 atm pressure. 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 to be considered at 1-atm pressure.

## 4. Analysis of the Heat-Capacity Data on Ruthenium, Rhodium, Palladium, Iridium, Osmium, and Platinum

The platinum metal elements have no heat-capacity measurements above about 20 K by modern methods with which accuracies of 0.1 or 0.2 percent can be achieved with reasonable care [29].

The literature heat-capacity data on ruthenium, rhodium, and iridium originated essentially from the same group of laboratories and cover separate regions

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of the temperature range 0 to 300 K with no overlap. (In the case of ruthenium, where two sets of measurements exist for the range 1 to 4 K, the values of heat capacity from two published sets of  $\gamma$  and  $\theta_D(0)$ [106, 31] differ from 8 to 12 percent.) Therefore, data from different laboratories were not available to make intercomparisons. The limits of uncertainty of the final selected values of heat capacity for these elements were estimated from measurements of these laboratories on other substances on which comparison with measurements of other laboratories have been made [29, 76].

The data on osmium are inadequate to present best values between 0 and 300 K. The sources of existing heat-capacity data only are presented.

The data on palladium and platinum, although more numerous, lack high-quality measurements on highpurity samples by modern techniques above 20 K. Most of the modern measurements are below 4 K. In the case of palladium, the only two extensive sets of measurements [19, 57] deviate from each other by about 1 percent between 100 and 300 K; other data below 50 K scatter widely. The scatter resulted probably from differences in the samples. Similarly, in the case of platinum, the only two extensive sets of measurements [17, 83] deviate systematically from each other, as much as 2 percent above 100 K and 7 percent below this temperature. Plots comparing values of  $\gamma$  and  $\theta_D(0)$  are given only for palladium and platinum.

#### 4.1. Ruthenium (Ru, Atomic Weight = 101.07) Assessment of Data Sources

From magnetic measurements Hulm and Goodman [36] found ruthenium to become superconducting at 0.47 K. The existing heat-capacity data are all above this temperature. The data analysis and the extrapolation of the values of heat capacity to zero K have been made on the basis of normal state ruthenium.

The selected values are based principally on the heatcapacity measurements reported by Clusius and Piesbergen [18], and by Ho and Viswanathan [31]. Since the upper limit of the measurements of Clusius and Piesbergen [18] was 272 K, the high-temperature relative-enthalpy measurements of Jaeger and Rosenbohm [44, 45] were analyzed to obtain the selected values in the region of 300 K. Figure 1 shows the deviations of the literature data from the selected values and the estimated limit of uncertainty of the selected values. Values selected for  $\gamma$  and  $\theta_D(0)$  are, respectively, 2.95  $\pm$  0.15 mJ/K<sup>2</sup> · mol and 530 $\pm$  30 K.

The data published by Dewar [23] (mean values between the normal boiling points of nitrogen and hydrogen) and by Holzmann [35] (relative enthalpy between 0 °C and temperatures up to 900 °C) were not considered in this analysis.

Wolcott [106] reported measurements between 1.2 and 20 K on a sample greater than 99.98 percent pure. A phosphorus-bronze thermometer was used in the liquid helium range and a constantan thermometer at higher temperatures. The thermometers were calibrated in terms of the 1948-<sup>4</sup>He scale [80, 94], hydrogen vapor pressure, and a helium gas thermometer. Wolcott fitted the data below 4 K to an equation of the form

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

and obtained

$$\gamma = 3.35 \text{ mJ/K}^2 \cdot \text{mol and } \theta_D(0) = 600 \text{ K};$$

he reported also

$$\theta_D(20) = 503 \, \text{K}.$$

The values of heat capacity based on these parameters were found to be inconsistent with the only existing extensive measurements to the higher temperatures of Clusius and Piesbergen [18]; the values are 6 to 12 percent higher than the selected values. The deviations are not plotted in figure 1. No weight was given to these data.

Clusius and Piesbergen [18] reported measurements between 11 and 272 K on a ruthenium sample for which no purity information is given. An isothermal jacket vacuum calorimeter was used in the measurements [14]. The temperatures were determined by means of a Pb-resistance thermometer. The temperatures were based on the calibration at the ice-point and vapor pressures of H<sub>2</sub> and 0<sub>2</sub> and on a table of resistance versus temperature for Pb previously obtained [19, 20]. These data are on the average within  $\pm$  0.2 percent of the selected values above 50 K but deviate as much as 6 percent below this temperature.

Ho and Viswanathan [31] reported measurements between 1.5 and 4.0 K on a sample of 99.98 percent purity prepared by arc-melting and casting into a cylinder. The 1958-<sup>4</sup>He vapor pressure scale [6] was employed in calibrating a carbon thermometer. Although the carbon thermometer was replaced by a germanium thermometer calibrated on the NBS Provisional Temperature Scale 2-20 (1965) [71], no measurements on pure ruthenium are shown above 4 K. By fitting the data to an equation of the form  $C = \gamma T + AT^3$ , the following data were reported:

$$\gamma = 2.95 \text{ mJ/K}^2 \cdot \text{mol and } \theta_P(0) = 530 \text{ K}.$$

The values of heat capacity based on these parameters are in close agreement with the selected values.

Jaeger and Rosenbohm [44, 45, 37] reported relative enthalpy measurements between 0 and 1604 °C on small spherical samples (Heraeus). A copper block receiving calorimeter was employed with thermocouples (copper versus constantan) for the determination of temperature change. The furnace temperature was determined with platinum versus platinum-rhodium thermocouples [39]. The heat capacity at 300 K derived from the enthalpy data is about 1.7 percent lower than the selected value.

The data of Clusius and Piesbergen [18] and of Jaeger and Rosenbohm [44, 45, 37] caused the  $\theta_D(T)$  curve to have an "upturn" around 270 K. More accurate data are needed to resolve values of heat capacity in this region.

#### 4.2. Rhodium (Rh, Atomic Weight = 102.905) Assessment of Data Sources

The selected values are based on the heat-capacity measurements reported by Wolcott [106], by Clusius and Losa [15, 16], and by Budworth, Hoare, and Preston [7]. Since the upper limit of the measurements of Clusius and Losa [15, 16] was 269 K, the relative-enthalpy measurements of Jaeger and Rosenbohm [43, 45] were analyzed to obtain the best values of heat capacity in the region of 300 K. Figure 2 shows the deviations of the literature data from the selected values and the estimated limit of uncertainty of the selected values. The values selected for  $\gamma$  and  $\theta_D(0)$ are, respectively, 4.65  $\pm$  0.15 mJ/K<sup>2</sup> mol and 512  $\pm$ 30 K.

The measurements obtained by Dewar [23] (mean values between the normal boiling points of nitrogen and hydrogen) and Holzmann [35] (relative enthalpy between 0 °C and temperatures up to 900 °C) were not considered in this analysis.

Wolcott [106] reported measurements between 1.2 and 20 K on a sample greater than 99.98 percent pure. Aphosphor-bronze thermometer was employed in the liquid helium range and a constantan thermometer at higher temperatures. The thermometers were calibrated in terms of the 1948-4He scale [80, 94], hydrogen vapor pressure, and a helium gas thermometer. Wolcott fitted the data below 4 K to the equation of the form

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

 $\gamma = 3.35 \text{ mJ/K}^2 \cdot \text{mol},$ 

and obtained

and

$$\theta_D(0) = 478 \, \mathrm{K}.$$

After subtracting the electronic term, 425 K was obtained for  $\theta_D(20)$ . The values of heat capacity based on these data are about 5 percent higher than the selected values.

Clusius and Losa [15, 16] reported measurements between 11 and 276 K on a sample (Heraeus) of 99.9 percent purity with traces of Fe, Ag, and Cu. An isothermal jacket vacuum calorimeter was used [14]. A Pb-resistance thermometer was employed, calibrated in terms of hydrogen and oxygen vapor pressure and the ice-point resistances. The intermediate temperatures were interpolated using temperature-resistance tables [79, 20] The data scatter over a wide range from the selected values.

· · ·			***								
	Temperature	Purity of	Electronic	Debye	Entropy a	t 298.15 K		Experime	ntal method		
Year	measurements K	Weight Percent	heat capacity, $\gamma$ mJ/K <sup>2</sup> · mol × 10 <sup>3</sup>	temperature, θ at 0 K K	J/K · mol	cal/K · mol	Calorimeter design	Thermometer	Temperature scale	Cooling of sample	References
1931	273-1877	?					MM–Cu	TC(Cu-Cn)	TC(Pt-Rh)		[45, 45]
1955	1.2-20	99.98	3350	600			VI–I	phosphor bronze, constantan	1948-4He, vp-H <sub>2</sub> , gas	cond	[106]
1959	11-272		$2590 \pm 210^{a}$	$\theta_D(10) = 505$	$28.53 \pm 0.21$ a	$6.82 \pm 0.05^{a}$	VI–I	Рь	Pb, vp-H2, vp-O2, gas	gas	[18]
1969	1.5–4.0	99.98	2950	530			VI–I	C, Ge	1958-4He, NBS (2–20 K)	MHS	[31]

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

<sup>a</sup>Figures prefixed with the ± symbols have been interpreted from the author's description to indicate the estimated uncertainties in the values given.



FIGURE 1. Deviations of the heat-capacity data of the literature on ruthenium from the selected values in the range 0 to 300 K. The estimated limit of accuracy, the temperature derivative,  $dC_p/dT$ , in  $J/K^2$  mol, and the Debye characteristic temperature  $\theta_D(T)$  of the selected values. (The values of  $\theta_D(T)$  were calculated from the relations  $C_v = C_p - \gamma T$  and  $D(\theta/T) = C_v/3R$ . See text for further details.) For the  $\theta_D(T)$  the vertical lines at 100 K and above correspond to 1 percent of the heat capacity and those below 100 K, 10 percent of the heat capacity.

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K	$\frac{C_p}{J/K \cdot mol}$	$\begin{array}{c} (H_T^\circ - H_0^c) \\ J/\mathrm{mol} \end{array}$	$\begin{array}{c} (H_T^\circ - H_0^c)/T \\ J/K \cdot mol \end{array}$	$\begin{array}{c c} (S_T^\circ - S_0^c) \\ J/K \cdot mol \end{array}$	$\begin{array}{c} -(G_{\tau}^{\circ}-H_{0}^{c})\\ \text{J/mol} \end{array}$	$\begin{array}{c c} -(G_T^\circ - H_0^\circ), \\ J/K \cdot mol \end{array}$
0.00	0.000000	0.000000	0.000000	0.000000	0.00000	0.00000
1.00	.00296	.00148	00148	00295	0.000000	0.00000
2.00	00600	00505	00208	00502	.00140	.00146
2.00	.00000	.00373	.00296	.00595	.00592	.00296
3.00	.00920	.0135	.00451	.00897	.0134	.00445
4.00	.0126	.0244	.00611	.0121	.0239	.00597
5.00	.0164	.0389	.00778	.0153	.0376	.00751
6.00	.0205	.0573	.00956	.0186	.0545	.00908
7.00	.0251	.0801	0114	0221	0749	0107
8.00	0303	108	0135	0258	0080	0194
9.00	.0361	.141	.0157	.0297	.127	.0124
10.00	0496	190	0100			
11.00	.0420	.180	.0180	.0339	.158	.0158
11.00	.0499	.220	.0206	.0383	.194	.0177
12.00	.0581	.280	.0234	.0429	.235	.0196
13.00	.0674	.343	.0264	.0480	.280	.0216
14.00	.0780	.416	.0297	.0533	.331	.0236
15.00	.0899	.499	.0333	.0591	387	0258
16.00	.103	.596	.0372	.0653		0200
17.00	.118	707	0416	0790	E10	.0281
18.00	126	.101	.0410	.0720	.510	.0305
10.00	.150	.033	.0403	.0793	.594	.0330
19.00	.155	.979	.0515	.0871	.677	.0356
20.00	.178	1.145	.0572	.0956	.768	.0384
25.00	.352	2.417	.0967	.152	1.376	0550
30.00	.676	4.914	.164	242	2 342	0781
35.00	1,186	9 4 9 0	271	382	2.012	.0701
40.00	1.878	17.09	.211	.302	5.010	.111
10.00	1.070	11.00	.421	.084	0.204	.157
45.00	2.727	28.53	.634	.852	9.825	.218
50.00	3.694	44.54	.891	1.189	14.90	.298
55.00	4.741	65.60	1.193	1.590	21.82	.397
60.00	5.830	92.02	1.534	2.049	30.89	515
65.00	6.930	123.9	1.907	2.559	42.39	.652
70.00	0.010	161.0				
70.00	8.012	101.3	2.304	3.112	56.55	.808
75.00	9.056	204.0	2.720	3.701	73.57	.981
80.00	10.05	251.8	3.147	4.317	93.60	1.170
85.00	11.00	304.4	3.581	4.955	116.8	1.374
90.00	11.89	361.6	4.018	5.609	143.2	1.591
95.00	12 72	423.2	4 455	6.975	172.0	1 820
100.00	13.51	488.8	4 999	6.047	905.0	2.050
105.00	10.01	400.0	4.000	0.947	205.9	2.059
110.00	14.24	601.1	5.510	7.024	242.4	2.308
115.00	14.92	707 4	5.738	8.303	282.2	2.565
			0.101	0.700	020.4	2.030
120.00	16.15	786.6	6.555	9.655	372.0	3.100
125.00	16.70	868.8	6.950	10.33	421.9	3.376
130.00	17.21	953.6	7.335	10.99	475.2	3.656
135.00	17.69	1041.	7.710	11.65	531.8	3.940
140.00	18.13	1130.	8.074	12.30	591.7	4.227
145.00	19 55	1999	0 499	10.04	654.9	4.536
150.00	10.00	1222.	0.420	12.94	004.0	4.510
155.00	10.73	1010.	0.112	13.30	(21.1	4.808
100.00	19.29	1411.	9.106	14.21	790.6	5.101
100.00	19.62	1509.	9.429	14.82	863.2	5.395
165.00	19.93	1608.	9.743	15.43	938.8	5.690
170.00	20.22	1708.	10.05	16.03	1018.	5 985
175.00	20.48	1810	10.00	16.69	1000	6 901
190.00	20.90	1010.	10.54	10.02	1099,	0.281
100.00	20.73	1913.	10.63	17.20	1184.	6.576
192.00	20.97	2017.	10.90	17.77	1271.	6.871
100			-			

TABLE 2. Thermodynamic properties of Ruthenium solid phase, atomic weight=101.07

T K	$\frac{C_p}{J/K \cdot mol}$	$(H_T^\circ - H_0^c)$ J/mol	$\frac{(H_T^\circ - H_0^c)/T}{J/K \cdot mol}$	$\begin{array}{c} (S_{\tau}^{\circ} - S_{0}^{c}) \\ \mathbf{J/K \cdot mol} \end{array}$	$\begin{array}{c c} -(C_T^\circ - H_0^c) \\ J/mol \end{array}$	$\frac{-(C_{T}^{\circ}-H_{0}^{\circ})/T}{J/K \cdot mol}$
195.00	21.41	2229.	11.43	18.89	1455.	7.459
200.00	21.61	2336.	11.68	19.43	1550.	7.752
205.00	21.80	2445.	11.93	19.97	1649.	8.043
210.00	21.99	2554.	12.16	20.50	1750.	8.333
215.00	22.17	2665.	12.39	21.02	1854.	8.622
220.00	22.34	2776.	12.62	21.53	1960.	8.910
225.00	22.51	2888.	12.84	22.03	2069.	9.196
230.00	22.67	3001.	13.05	22.53	2180.	9.480
235.00	22.82	3115.	13.26	23.02	2294.	9.763
240.00	22.96	3229.	13.46	23.50	2411.	10.04
245.00	23.10	3345.	13.65	23.98	2529.	. 10.32
250.00	23.22	3460.	13.84	24.44	2650.	10.60
255.00	23.34	3577.	14.03	24.90	2774.	10.88
260.00	23.45	3694.	14.21	25.36	2899.	11.15
265.00	23.55	3811.	14.38	25.81	3027.	11.42
270.00	23.65	3929.	14.55	26.25	3157.	11.69
273.15	23.71	4004.	14.66	26.52	3241.	11.86
275.00	23.74	4048.	14.72	26.68	3290.	11.96
280.00	23.82	4167.	14.88	27.11	3424.	12.23
285.00	23.89	4286.	15.04	27.53	3561.	12.49
290.00	23.96	4406.	15.19	27.95	3700.	12.76
295.00	24.02	4525.	15.34	28.36	3840.	13.02
298.15	24.06	4601.	15.43	28.61	3930.	13.18
300.00	24.08	4646.	15.49	28.76	3983.	13.28

TABLE 2. Thermodynamic properties of Ruthenium solid phase, atomic weight = 101.07 - Continued

 $H_{\delta}$  and  $S_{\delta}$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

Budworth, Hoare, and Preston [7] reported measurements from 1.8 to 4.2 K on a "spectroscopically standardized" sample of rhodium in which the impurities were of the order of 2 or 3 ppm. Cooling of the sample was achieved by condensing liquid helium in a small chamber attached to the sample vessel and subsequently removing the helium by pumping. A carbonresistance thermometer calibrated on the 1955L-<sup>4</sup>He scale [92, 93] was used in the measurements of temperatures. By fitting the data to an equation of the form

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

the above authors reported:

$$\gamma = 4.65 \pm 0.018 \text{ mJ/K}^2 \cdot \text{mol and } \theta_D(0) = 512 \pm 17 \text{ K}.$$

The values of heat capacity based on these data are in close agreement with the selected values.

Jaeger and Rosenbohm [43, 45, 37] reported relativeenthalpy measurements between 0 to 1604 °C on the "purest rhodium from Heraeus". A copper block receiving calorimeter was employed with copper versus constantan thermocouples for the measurement of temperature change [392]. Platinum versus platinumrhodium thermocouples were used for determining the furnace temperature. At 300 K, the heat capacity derived from the relative-enthalpy data is about 3 percent higher than the selected value.

### 4.3. Palladium (Pd, Atomic Weight = 106.4) Assessment of Data Sources

The data on palladium scatter widely. The selected values of heat capacity are based mostly on the measurements reported by Clusius and Schachinger [19]. Hoare and Yates [32], Mackliet and Schindler [56]. Mitachek and Aston [57], and Veal and Rayne [95]. The high-temperature data that were analyzed to select the best values around 300 K are those reported by Jaeger and Rosenbohm [42, 45], Jaeger and Veenstra [49, 38], and Vollmer and Kohlhass [99]. Figures 4 and 5 show the deviations of the literature data from the selected values; the estimated limit of uncertainty of the selected values is  $\pm 0.6$  percent between 33 and 300 K and is ±1 percent below 33 K. To maintain a simple  $\theta_d(T)$  curve the selected values of heat capacity from 20 to 30 K deviate generally from the experimental data. (See figure 5). Published values of  $\gamma$  and  $\theta_D(0)$  are compared in figure 3; the selected values are  $\gamma = 9.40 \pm 0.09$  mJ/K<sup>2</sup> · mol and  $\theta_d(0) = 274.5 \pm$ 2.5 K.

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

	Temperature	Purity of	Electronic	Debye	Entropy #	ut 298.15 K		Experime	ental method		T
Year	measurements K	Weight Percent	heat capacity, $\gamma$ mJ/K <sup>2</sup> · mol × 10 <sup>3</sup>	temperature, θ at 0 K K	J/K · mol	cal/K · mol	Calorimeter design	Thermometer	Temperature scale	Cooling of sample	References
1931	273-1877	?		I			MM-Cu	TC(Cu-Cn)	TC(Pt-Rh)		[43, 45]
1955	1.2-20	99.98	4900	478			VI-I	phosphor bronze, constantan	1948- <sup>4</sup> Не, vp-H <sub>2</sub> , gas	cond	[106]
1955	10-269	99.9	4180	$\theta_D(10) = 450$	31.63	7.56	VI-I	РЪ	Pb, vp-H <sub>2</sub> vp-O <sub>2</sub>	gas	[15, 16]
1960	1.8-4.2	"spectroscopi- cally stand- ardized"	4650±18°	512±17 °			VI-I	C	1955L-4He	cond	[7]

\* Figures prefixed with the ± symbols have been intrepreted from the authors' description to indicate the precision of the values given.





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		-	-			
Т	$C_p$	$(H_{\tau}^{\circ} - H_{\alpha}^{c})$	$(H_m^\circ - H_n^c)/T$	$(S^{\circ}_{-} - S^{\circ}_{-})$	$-(G^{\circ}-H^{\circ})$	$-(G^{\circ}-H^{\circ})/T$
K	J/K mol	J/mol	J/K · mol	$J/K \cdot mol$	I/mol	$I/K \cdot mol$
0.00	0.000000	0.000000	0.000000	0,00000		
0.00	0.00000	0.00000	0.000000	0.00000	0.000000	0.00000
1.00	.00400	.00233	.00233	.00465	.00233	.00233
2.00	.00942	.00936	.00468	.00934	.00932	.00466
3.00	.0143	.0212	.00707	.0141	.0210	.00701
4.00	.0195	.0381	.00953	.0189	.0375	.00938
5 00	0053			·		
5.00	.0251	.0604	.0121	.0239	.0589	.0118
6.00	.0311	.0884	.0147	.0289	.0853	.0142
7.00	.0376	.123	.0175	.0342	.117	.0167
8.00	.0450	.164	.0205	.0397	.154	.0192
9.00	.0533	.213	.0237	.0455	.196	.0218
10.00	0.000					
10.00	.0629	.271	.0271	.0516	.245	.0245
11.00	.0738	.339	.0308	.0581	.300	.0272
12.00	.0863	.419	.0349	.0650	.361	.0301
13.00	.101	.512	.0394	.0725	.430	.0331
14.00	.117	.621	.0444	.0805	.506	.0362
						1
15.00	.136	.747	.0498	.0892	.591	.0394
16.00	.158	.894	.0559	.0987	.685	.0428
17.00	.183	1.064	.0626	.109	.789	.0464
18.00	.212	1.262	.0701	.120	.903	.0502
19.00	.245	1.490	.0784	.133	1.030	.0542
20.00	.284	1.754	.0877	.146	1.169	.0585
25.00	.577	3.824	.153	.237	2.109	.0844
30.00	1.090	7.896	.263	.384	3.636	.121
35.00	1.814	15.08	.431	.604	6.075	.174
40.00	2.740	26.38	.659	.905	9.813	.245
45.00	3.842	42.78	.951	1.290	15.26	.339
50.00	5.040	64.96	1.299	1.756	22.85	.457
55.00	6.264	93.22	1.695	2.294	32.94	.599
60.00	7.466	127.6	2.126	2.891	45.88	.765
65.00	8.625	167.8	2.582	3.534	61.93	.953
	and the second					
70.00	9.731	213.7	3.053	4.214	81.29	1.161
75.00	10.78	265.0	3.534	4.922	104.1	1.388
80.00	11.77	321.4	4.018	5.650	130.5	1.632
85.00	12.70	382.6	4.501	6.391	160.6	1.890
90.00	13.56	448.3	4.981	7.142	194.5	2.161
95.00	14.37	518.1	5.454	7.897	232.1	2.443
100.00	15.11	591.8	5.918	8.653	273.4	2.734
105.00	15.80	669.2	6.373	9.407	318.0	3.034
110.00	16.44	749.8	6.816	10.16	367.5	3.341
115.00	17.03	833.5	7.248	10.90	420.2	3.653
120.00	17.58	920.0	7.667	11.64	476.5	3.971
125.00	18.09	1009.	8.074	12.37	536.5	4.292
130.00	18.55	1101.	8.468	13.08	600.1	4.616
135.00	18.99	1195.	8.850	13.79	667.3	4,943
140.00	19.39	1291.	9.219	14.49	738.1	5.272
145.00	19.77	1389.	9.577	15.18	812.2	5.602
150.00	20.12	1488.	9.922	15.85	889.8	5.932
155.00	20.45	1590.	10.26	16.52	970.8	6.263
160.00	20.75	1693.	10.58	17.17	1055.	6.594
165.00	21.04	1797.	10.89	17.82	1142.	6.924
170.00	21.31	1903.	11.19	18.45	1233.	7.254
175.00	21.56	2010.	11.49	19.07	1327	7.583
180.00	21.80	2119	11.77	19.68	1424	7,910
185.00	22 02	2228	12.04	20.28	1524	8 236
190.00	22.02	2330	12.01	20.20	1627	8 561
190.00	22.23	2339.	12.31	20.87	1627.	8.561

TABLE 4. Thermodynamic properties of Rhodium solid phase, atomic weight=102.905

T K	C <sub>p</sub> ∙ J/K · mol	$(H_T^\circ - H_0^c)$ J/mol	$\frac{(H_T^\circ - H_0^c)/T}{J/K \cdot mol}$	$(S_T^\circ - S_0^c)$ J/K · mol	$\frac{-(G_{T}^{\circ}-H_{0}^{c})}{J/\mathrm{mol}}$	$\frac{-(G_T^\circ - H_0^\circ)/T}{J/K \cdot mol}$
195.00	22.43	2451.	12.57	21.45	1732.	8.884
200.00	22.62	2563.	12.82	22.02	1841.	9.206
205.00	22.80	2677.	13.06	22.58	1953.	9.525
210.00	22.97	2791.	13.29	23.13	2067.	9.842
215.00	23.14	2906.	13.52	23.68	2184.	10.16
220.00	23.29	3023.	13.74	24.21	2304.	10.47
225.00	23.44	3139.	13.95	24.74	2426.	10.78
230.00	23.58	3257.	14.16	25.25	2551.	11.09
235.00	23.71	3375.	14.36	25.76	2679.	11.40
240.00	23.84	3494.	14.56	26.26	2809.	11.70
245.00	23.96	3614	14.75	26.75	2941.	12.00
250.00	24.07	3734	14.93	27.24	3076.	12:30
255.00	24.18	3854.	15.11	27.72	3214.	12.60
260.00	24.28	3975.	15.29	28.19	3353.	12.90
265.00	24.38	4097.	15.46	28.65	3495.	13.19
270.00	94.47	4210.	15.63	29 11	3640	13.48
273.15	24.52	4296.	15.73	29.39	3732.	13.66
275.00	24.55	4342.	15.79	29.56	3786.	13.77
280.00	24.64	4465.	15.95	30.00	3935.	14.05
285.00	24.71	4588.	16.10	30.44	4086.	14.34
290.00	94.79	4712	16.25	30.87	4240	14.62
295.00	24.86	4836	16.39	31.29	4395.	14.90
223.00	24.00	4914	16.48	31.56	4494	15.07
300.00	24.93	4960.	16.53	31.71	4553.	15.18

TABLE 4. Thermodynamic properties of Rhodium solid phase, atomic weight = 102.905 - Continued

 $H_{a}^{c}$  and  $S_{a}^{c}$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

The data that were not considered in the analysis are those reported by: Violle [97] (relative enthalpy between 0 °C and temperatures up to 1265 °C), Pionchon [70] (relative enthalpy between 0 °C and temperatures up to 1048 °C), Behn [3] (mean values between 18 °C and 100, -79, and -186 °C), Richards and Jackson [77] (mean values between 20 °C and -188 and 100 °C), Dewar [23] (mean values between the boiling points of nitrogen and hydrogen), and Holzmann [35] (relative enthalpy between 0 °C and temperatures up to 904 °C). Nace and Aston [59] reported measurements on palladium black between 15 and 345 K. Their data were not used in this analysis.

Pickard and Simon [67, 69] reported measurements between 2 and 22 K on a palladium sample of unspecified purity. When the sample was "strongly heated" in vacuum, the hydrogen that was desorbed was "scarcely detectable". An isothermal jacket vacuum calorimeter was used in the measurements. The sample was cooled by condensing the refrigerant (liquid  $H_2$  or He) in the sample vessel and subsequently removing it by pumping. Temperatures were determined by means of a "Eureka" wire thermometer calibrated in terms of the vapor pressures of helium and hydrogen [68]. Pickard and Simon fitted the data between 2 and 22 K, to an equation of the form

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

and obtained

#### $\gamma = 13.0 \text{ mJ/K}^2 \cdot \text{mol and } \theta_D(0) = 275 \text{ K}.$

The values of heat capacity calculated from these values of  $\gamma$  and  $\theta_d(0)$  are over 20 percent higher than the selected values. The value of  $\gamma$  is exceptionally high. The smoothed values of heat capacity given in the paper are also higher than the selected values, +29 percent at 2 K to -0.8 percent at 20 K. The data were given very little weight in the analysis.

Clusius and Schachinger [19] reported measurements between 14 and 268 K on a sample from Heraeus of the "highest purity". An isothermal jacket vacuum calorimeter and Pb resistance thermometer were employed [14, 79, 20]. The data are on the average within about 0.5 percent of the selected values above 50 K but deviate as much as 9 percent below this temperature.

Rayne [74] reported measurements on a palladium sample of 99.98 percent purity from 0.2 to 1 K. In the experimental method, the sample was attached to a paramagnetic salt ( $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$ ) through a heavy gage copper wire and a copper vane embedded in the salt. The salt was used for adiabatic-demagnetization cooling of the sample and for the measurement of temperature. The 1948-4He scale [80, 90] was employed in calibrating 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 values of the observed heat capacity 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 (10.7±0.5 mJ/K<sup>2</sup>· mol) is higher than most of the published values.

Rayne [75] in a later publication reported measurements between 1.5 and 4.1 K on a sample of palladium wire of purity greater than 99.999 percent, the impurities of Cu, Ag, Fe, Ca, Mg, and Si each being less than 1 ppm. The 1955E-<sup>4</sup>He [12, 13] vapor-pressure scale was employed. Measurements were first made in the strained state (a condition after coiling the wire sample) and after annealing at 600 °C. Then a second sample of 99.98 percent purity on which measurements were obtained earlier [74] was investigated again. The measurements on the first sample in both the strained and annealed states are stated to agree within the experimental error. Rayne fitted the data on the first sample to an equation of the form

and obtained

$$\gamma = 9.87 \pm 0.11^3 \text{ mJ/K}^2 \cdot \text{mol}$$

and

$$\theta_{\rm D}(0) = 299 \pm 12^3 \, {\rm K}.$$

 $C = \gamma T + AT^3$ 

The data on the second sample yielded

and

.

 $\gamma = 9.64 \pm 0.08^3 \text{ mJ/K}^2 \cdot \text{mol}$ 

 $\theta_D(0) = 297 \pm 9^3 \,\mathrm{K}.$ 

These values for  $\gamma$  are considerably lower than that of the earlier measurements [74]. The published observed heat-capacity data are as much as 6 percent higher than the selected values.

In another set of measurements, Veal and Rayne [95] reported measurements between 1.4 and 86 K on a palladium sample stated to be identical to that investigated by Hoare and Yates [32]. (See below.) The calorimeter was operated by the isothermal shield method. A germanium thermometer was employed. In the liquid helium range the thermometer was calibrated in terms of the 1958-<sup>4</sup>He vapor pressure scale [6]; at the higher temperatures the thermometer was calibrated in terms of a calibrated laboratory standard germanium thermometer. Veal and Rayne fitted the data below 4.2 K to an equation of the form

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

and obtained

$$\gamma = 9.42 \pm 0.02 \text{ mJ/K}^2 \cdot \text{mol and } \theta_D(0) = 273.6 \pm 1.4 \text{ K}.$$

The published observed heat-capacity data deviate as much as 10 percent from the selected values; however, the values of heat capacity between 1.4 and 4.2 K based on the above  $\gamma$  and  $\theta_D(0)$  are about 0.2 percent higher than the selected values.

Hoare and Yates [32] reported measurements between 2 and 4.2 K on a specimen of impurity content shown by spectrographic analysis to be less than "faint", except for silver which was found to be "fairly strong". The 1955L-<sup>4</sup>He [92, 93] vapor pressure scale was employed. Hoare and Yates fitted the data to an equation of the form

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

and obtained

and

$$\gamma = 9.31 \pm 0.05 \text{ mJ/K}^2 \cdot \text{mol}$$

$$\theta_D(0) = 274 \pm 3 \text{ K}.$$

The values of heat capacity based on these data are about 0.8 to 0.9 percent lower than the selected values. Hoare and Yates [32] state that P. L. Smith (Clarendon Laboratory) obtained  $\gamma = 9.25$  mJ/K<sup>2</sup> mol on the same sample.

Crangle and Smith [21] reported heat-capacity measurements between 78 and 105 K on a sample of 99.96 percent purity. No numerical data or description of the apparatus is reported. However, a plot of the data that is given shows about 1 to 1.5 percent scatter. The mean of the data is about 1 to 2 percent higher than those reported by Clusius and Schachinger [19] which are in turn within  $\pm 0.5$  percent of the selected values.

Mackliet and Schindler [56] reported, as a part of their heat-capacity investigations on Ni-Pd alloys, measurements on "high-purity" palladium between 1.5 and 4.2 K. Helium exchange gas was used in cooling. Temperatures were determined by means of a carbon resistance thermometer calibrated in terms of the 1958-<sup>4</sup>He vapor-pressure scale [6]. Mackliet and Schindler fitted the data to an equation of the form

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

and obtained

$$\gamma = 9.38_5 \pm 0.03_5 \text{ mJ/K}^2 \cdot \text{mol and } \theta_D(0) = 272 \pm 3 \text{ K}.$$

The values of heat capacity based on these values of  $\gamma$  and  $\theta_D(0)$  are within 0.2 percent of the selected values.

Mitacek and Aston [57] reported measurements on "high-purity" palladium from 30 to 278 K. An adiabatic vacuum calorimeter was used with helium exchange gas for cooling. The temperatures were determined by means of a platinum resistance thermometer cali-

<sup>&</sup>lt;sup>3</sup>Random and systematic error estimated at 99 percent confidence level by Rayne [75].

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<u></u>	Temperature	Purity of	Electronic	Debye	Entropy a	Entropy at 298.15 K		Experimental method			
Year	range of heat measurements K	specimen Weight Percent	coefficient of heat capacity, $\gamma$ mJ/K <sup>2</sup> · mol × 10 <sup>3</sup>	characterístic temperature, θ at 0 K K	J/K · mol	cal/K · mol	Calorimeter design	Thermometer	Temperature scale	Cooling of sample	References
1930	273-1810	?					MM-Cu	TC(Cu-Cn)	TC(Pt-Rh)		[42, 45]
1 <b>934</b>	273-1772	?					MM-Cu	TC(Cu-Cn)	TC(Pt-Rh)		[49, 38]
1 <b>936</b>	2-22	. ?	13000	275	37.85 <sup>a</sup>	9.05 ª	VA-I	"Eureka"	vp-4He, vp-He gas	gas	[67, 69]
1 <b>947</b>	14-268	"highest purity"	13000	$\theta_D(20) = 279$	37.82	9.04	VI-I	РЬ	Pb vp-H <sub>2</sub> , vp-O <sub>2</sub> gas	gas	[19]
1954	0.2-1	99.98	10700±540 °				VI-I	MS	MS, 1948-4He	gas AD–MC	[74]
1957	1.5-4.1	99,999	9870 ± 110 b	299±12 °			VI-I	С	1955E- <sup>4</sup> He	gas	[75]
1957	1.5-4.1	99.98	9640±80 <sup>ь</sup>	297±9 b			VI-I	С	1955E- <sup>4</sup> He	gas	[75]
1957	2-4.2	"spectroscopi- cally stand- ardized"	9310±50 °	274±3°			VI-I	С	1955L-⁴ He	cond	[32]
1963	1.5-4.2	"highest purity"	9385±35 °	272±3°			VI-I	С	1958- <sup>4</sup> He	gas	[56]
1963	30-278	"highest purity"					VA-I	Pt	IPTS-48	gas	[57]
1964	1.4-86	"spectroscopi- cally stand- ardized"	9420 ± 20 °	273.6±4 °			VI-I	Ge	1958-4He, "lab standard"	gas	[95]
1965	1.3-30	99,999	9570 ± 70 °	267 ± 8 °			VI-I	С	1958-4He vp-H2	gas	[5]
1969	300-1825	99.96					СН	TC(Pt-Rh)	TC(Pt-Rh)		[99]

## TABLE 5. Sources of heat-capacity data on palladium used in the analysis

<sup>a</sup> Interpolated from the table of thermodynamic functions given by Pickard and Simon [69].

<sup>b</sup> Figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the estimated uncertainties in the values given.

<sup>c</sup> Figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the precision of the values given.

THERMODYNAMIC PROPERTIES OF TRANSITION ELEMENTS



FIGURE 3. Comparison of the reported values of electronic coefficients of heat capacity,  $\gamma$ , and Debye characteristic temperatures,  $\theta_D(0)$ , of palladium. The figures (without decimal) along the horizontal lines indicate literature references in section 5





For the  $\theta_2(T)$  the vertical lines at 100 K and above correspond to 1 percent of the heat capacity and those below 100 K. 10 percent of the heat capacity.

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FIGURE 5. Deviations of the heat-capacity data of the literature on palladium from the selected values in the range 0 to 30 K.

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TABLE 6.	Thermodynamic properties of Palladium solid phase, atomic weight=106.4

T K	C <sub>p</sub> J/K · mol	$(H_T^\circ - H_0^c)$ J/mol	$\frac{(H_T^\circ - H_0^c)/T}{J/K \cdot mol}$	$(S_T^\circ - S_0^c) \\ J/K \cdot mol$	$\begin{array}{c c} -(G_T^\circ - H_0^c) \\ J/\mathrm{mol} \end{array}$	$\begin{vmatrix} -(G_T^\circ - H_0^c)/T \\ J/\mathbf{K} \cdot \mathrm{mol} \end{vmatrix}$
	0.000000	0.000000	0.000000	0.00000	0.000000	0.00000
0.00	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1.00	.00949	.004/2	.00472	.00945	.00471	.00471
2.00	.0196	.0192	.00959	.0191	.0109	.00940
3.00	.0307	.0442	.0147	.0290	.0429	.0143
4.00	.0436	.0812	.0203	.0396	.0772	.0193
5.00	.0587	.132	.0264	.0509	.122	.0245
6.00	.0767	.200	.0333	.0632	.179	.0299
7.00	.0981	.287	.0410	.0765	.249	.0356
8.00	124	.397	.0497	.0913	.333	.0416
9.00	.155	.536	.0595	.108	.432	.0480
10.00	100	700	0709	196	E40	0540
10.00	.192	.708	.0708	.120	.549	.0549
11.00	.236	.922	.0838	.146	.084	.0622
12.00	.288	1.183	.0986	.169	.841	.0701
13.00	.348	1.500	.115	.194	1.023	.0787
14.00	.417	1.882	.134	.222	1.230	.0879
15.00	.495	2.337	.156	.254	1.468	.0979
16.00	.581	2,874	.180	.288	1.739	.109
17 00	676	3 502	206	326	2.046	120
18.00	780	4.990	235	368	2.010	133
19.00	.894	5.065	.267	.413	2.783	.146
20.00	1.018	6.020	.301	.462	3.220	.161
25.00	1.791	12.93	.517	.767	6.250	.250
30.00	2.816	24.35	.812	1.181	11.07	.369
35.00	4.038	41.42	1.184	1.705	18.24	.521
40.00	5.376	64.93	1.623	2.331	28.29	.707
45.00	6 761	95.97	9 117	3 044	41 70	027
50.00	8 139	132.5	2.111	3 828	58.85	1 177
55.00	0.159	176.6	2.001	1 666	90.05	1.111
55.00	9.409	170.0	3.210	4.000	205.00	1.450
65.00	10.75	227.1	3.705	6 450	105.0	2.085
00.00	11.50	200.1		0.100	100.0	2.000
70.00	12.98	345.9	4.942	7.372	170.1	2.430
75.00	13.97	413.3	5.511	8.301	209.3	2.790
80.00	14.88	485.5	6.068	9.232	253.1	3.164
85.00	15.71	562.0	6.611	10.16	301.6	3.548
90.00	16.47	642.5	7.138	11.08	354.7	3.941
05.00	17.17	796.6	7.640	11.00	410.4	4.943
95.00	17.17	/20.0	1.048	11.99	412.4	4.341
100.00	17.82	814.1	8.141	12.89	4/4.0	4.146
105.00	18.41	904.7	8.616	13.77	541.2	5.154
110.00	18.96	998.1	9.074	14.64	612.3	5.566
115.00	19.46	1094.	9.515	15.49	687.6	5.979
120.00	19.93	1193.	9.939	16.33	767.2	6.393
125.00	20.36	1293.	10.35	17.15	850.9	6.807
130.00	20.30	1906	10.74	17.06	028 7	7 221
135.00	20.10	1590.	10.74	10.75	1090	7.622
140.00	21.13	1609	11.12	10.13	1000.	0.044
140.00	21.47	1000.	11.40	19.55	1120.	0.044
145.00	21.78	1716.	11.83	20.29	1226.	8.453
150.00	22.07	1825.	12.17	21.03	1329.	8.860
155.00	22.34	1936.	12.49	21.76	1436.	9.264
160.00	22.59	2049.	12.80	22.47	1547.	9.666
165.00	22.83	2162.	13.10	23.17	1661.	10.06
180.00			10.00			10.15
170.00	23.05	2277.	13.39	23.85	1778.	10.46
175.00	23.25	2393.	13.67	24.52	1899.	10.85
180.00	23.44	2509.	13.94	25.18	2023.	11.24
185.00	23.63	2627.	14.20	25.83	2151.	11.63
	00.00	0746	1 14 45	96.46	0000	19.01

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T	<i>C</i> <sub><i>p</i></sub>	$(H_T^\circ - H_0^c)$	$(H_{\tau}^{\circ} - H_{\theta}^{c})/T$	$(S_{\tau}^{\circ}-S_{0}^{c})$	$-(G_{\tau}^{\circ}-H_{\rho}^{c})$	$-(G_r^\circ - H_o^c)/T$
K	J/K · mol	J/mol	J/K · mol	J/K ∙ mol	J/mol <sup>"</sup>	J/K ∙ mol
195.00	23.96	2865.	14.69	27.08	2416.	12.39
200.00	24.11	2985.	14.93	27.69	2552.	12.76
205.00	24.26	3106.	15.15	28.29	2692.	13.13
210.00	24.39	3228.	15.37	28.87	2835.	13.50
215.00	24.52	3350.	15.58	29.45	2981.	13.87
000.00	24.64	0.470	15 50			14.00
220.00	24.64	3473.	15.79	30.01	3130.	14.23
225.00	24.76	3597.	15.98	30.57	3281.	14.58
230.00	24.87	3721.	16.18	31.11	3435.	14.94
235.00	24.97	3845.	16.36	31.65	3592.	15.29
240.00	25.07	3970.	16.54	32.18	3752.	15.63
045.00	05.16	4007	16.70	30.00	0014	15.00
245.00	25.10	4096.	16.72	32.69	3914.	15.98
250.00	25.25	4222.	16.89	33.20	4079.	16.32
255.00	25.33	4348.	17.05	33.70	4246.	16.65
260.00	25.41	4475.	17.21	34.20	4416.	16.98
265.00	25.48	4602.	17.37	34.68	4588.	17.31
270.00	25.55	4730	17 59	35.16	4763	17 64
273.15	25.59	4811	17.61	35.45	4874	17.84
275.00	25.62	4858	17.67	35.63	4040	17.04
280.00	25.62	4086	17.81	36.00	5110	18.99
285.00	25.00	5115	17.01	36.54	5201	18.60
200.00	20.14	5115.	11.55	50.54	5501.	10.00
290.00	25.80	5244.	18.08	36.99	5484.	18.91
295.00	25.86	5373.	18.21	37.43	5670.	19.22
298.15	25.89	5454.	18.29	37.71	5789.	19.42
300.00	25.91	5502.	18.34	37.87	5859.	19.53

TABLE 6. Thermodynamic properties of Palladium solid phase, atomic weight=106.4-Continued

 $H_0^c$  and  $S_0^c$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

brated on the Pennsylvania State University scale [58] and the International Practical Temperature Scale of 1948 [84, 85]. The deviation of their observed data from the selected values are on the average within  $about \pm 0.5$  percent.

Boerstoel, du Chatenier, and van den Berg [5] reported measurements between 1.3 and 30 K on 99.999 percent pure sample, principal impurities being 0.0002 percent each of iron and silicon. The temperatures, measured by means of a carbon resistance thermometer, were based on the 1958-<sup>4</sup>He scale [6] and the hydrogen vapor pressure work of Hoge and Arnold [33]. Helium exchange gas was used in cooling. The above authors fitted the data below 5 K to an equation of form

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

and obtained

$$\gamma = 9.57 \pm 0.07 \text{ mJ/K}^2 \cdot \text{mol and } \theta_D(0) = 267 \pm 8 \text{ K}.$$

No other numerical data are given. The values of heat capacity based on these values of  $\gamma$  and  $\theta_D(0)$  are over 2 percent higher than the selected values.

Jaeger and Rosenbohm [42, 45, 37] reported relative enthalpy measurements between 0 and 1537 °C on a powder sample from Heraeus melted into small spheres. A copper block receiving calorimeter was employed [39]. The values of heat capacity around 300 K derived from the data are about 5 to 6 percent lower than the selected values.

Jaeger and Veenstra [49, 38] repeated the earlier relative enthalpy measurements of Jaeger and Rosenbohm [42, 45, 37] after annealing the palladium sample and improving the temperature measurements. The value of heat capacity derived from these data is about 2 percent higher than the selected value at 300 K.

Vollmer and Kohlhaas [99] reported measurements between 300 and 1825 K on a sample of 99.96 percent purity employing a continuous heating method. The values of heat capacity derived from the data are about 2 to 3 percent lower than the expected values in the neighborhood above 300 K.

### 4.4. Osmium (Os, Atomic Weight = 190.2) Assessment of Data Sources

The heat-capacity data on osmium are inadequate to obtain best values between 0 and 300 K. The available data are only the values of  $\theta_D(0)$ ,  $\gamma$ , and  $\theta_D(20)$  based on measurements between 1.2 and 20 K [106], the mean heat capacity between the normal boiling points of nitrogen and hydrogen [23], and the high-temperature relative-enthalpy measurements between 0 and 1604

°C of Jaeger and Rosenbohm [43]. No analysis of the data on osmium is, therefore, presented in this monograph. The following is a brief description of the available data.

Hulm and Goodman [36] found osmium to become superconducting at 0.71 K.

Dewar [23] determined the mean heat capacity of osmium between the normal boiling temperatures of nitrogen and hydrogen employing a hydrogen vaporization calorimeter.

Wolcott [106] reported measurements between 1.2 and 20 K on a sample greater than 99.98 percent pure. A phosphor-bronze thermometer was used in the liquid helium range and a constantan thermometer at higher temperatures. The thermometers were calibrated in terms of 1948-<sup>4</sup>He scale [80, 94], hydrogen vapor pressure, and a helium gas thermometer. Wolcott fitted the data below 4 K to the equation of the form

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

and obtained  $\gamma = 2.35 \text{ mJ/K}^2 \cdot \text{mol}$  and  $\theta_D(0) = 500 \text{ K}$ ; he reported also  $\theta_D(20) = 410 \text{ K}$ .

Jaeger and Rosenbohm [43] reported relative enthalpy measurements between 0 and 1604 °C on the "purest osmium from Heraeus".

### 4.5. Iridium (Ir, Atomic Weight = 192.2) Assessment of Data Sources

The selected values are based on heat-capacity measurements reported by Wolcott [106] and by Clusius and Losa [15, 16]. Since the upper limit of the measurements of Clusius and Losa [15, 16] was 276 K, the hightemperature relative-enthalpy measurements of Jaeger and Rosenbohm [44] and of Wöhler and Jochum [105] were used in the selection of the best values of heat capacity in the region of 300 K. The uncertainty of the final selected values was estimated on the basis of the analysis of measurements on other substances reported by Wolcott and by Clusius and his collcagues [29, 76]. Figure 6 shows the deviations of their data from the selected values and the estimated limit of uncertainty of the selected values. Values selected for  $\gamma$  and  $\theta_D(0)$  are, respectively,  $3.20 \pm 0.10 \text{ mJ/K}^2 \cdot \text{mol}$ and  $420 \pm 10$  K.

The following measurements were not considered in the analysis: Violle [98] (relative enthalpy between 0 °C and temperatures up to 1400 °C, Behn [3] (mean values between 18 °C and 100, -79, and -186 °C and a sample of 99.8 percent Ir and 0.15 percent Pt), and Dewar [23] (mean values between the normal boiling points of nitrogen and hydrogen).

Wolcott [106] reported measurements between 1.2 and 20 K on a sample greater than 99.98 percent pure. A phosphor-bronze thermometer was used in the liquid helium range and a constantan thermometer at higher temperatures. The thermometers were calibrated in terms of 1948-<sup>4</sup>He scale [80, 94], hydrogen vapor pressure, and a helium gas thermometer. Wolcott fitted the data below 4 K to the equation of the form

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

and obtained  $\gamma = 3.14 \text{ mJ/K}^2 \cdot \text{mol}$  and  $\theta_D(0) = 420 \text{ K}$ . Wolcott reported also  $\theta_D(20) = 350 \text{ K}$ . The data are about 10 to 12 percent higher than the selected values.

Clusius and Losa [15, 16] reported measurements between 11 and 276 K on a sample (Heraeus) of 99.9 percent purity with traces of Fe, Ag, and Cu. A Pbresistance thermometer was employed, calibrated in terms of hydrogen and oxygen vapor pressures and the ice-point resistance [79, 20]. The values reported for  $\gamma$  and  $\theta_D(10)$  are, respectively, 3.51 mJ/K<sup>2</sup> · mol and 430 K. The observed data are on the average within about  $\pm$  0.3 percent of the selected values above 50 K but deviate up to 6 percent below this temperature.

Andres and Jensen [1] reported unpublished measurements of M. Dixon and colleagues (Leeds);  $\gamma - 3.27$  mJ/K<sup>2</sup> · mol and  $\theta_D(0) = 425$  K. These parameters yield values of heat capacity about 1 to 2 percent higher than the selected values.

Jaeger and Rosenbohm [44, 45, 37] reported relative enthalpy measurements between 0 and 1535 °C on the "purest iridium from Heraeus" in the form of peasize globulets. A copper block receiving calorimeter was employed with thermocouples for measuring the temperature changes [39]. The heat capacity at 300 K derived from the enthalpy data is 0.2 percent lower than the selected value.

Wöhler and Jochum [105] reported relative enthalpy measurements between 16 and 1000 °C. The heat capacity at 300 K derived from the data is about 4 percent higher than the selected value.

### 4.6. Platinum (Pt, Atomic Weight = 195.09) Assessment of Data Sources

The selected values are based largely on the measurements reported by Clusius, Losa, and Franzosini [17]; by Dixon, Hoare, Holden, and Moody [25]; by Dixon, Hoare, and Holder [24], by Shoemake and Rayne [82]; and by Berg [4]. The high-temperature relative-enthalpy measurements of White [101, 102, 103]; of Wüst, Meuthen, and Durrer [1072; of Jaeger, Rosenbohm, and Bottema [41, 40, 47, 48, 46]; and of Kendall, Orr, and Hultgren [51] were given the most weight in obtaining the selected values of heat capacity in the region of 300 K. Figures 8 and 9 show the deviations of the literature data from the selected values. The estimated limit of uncertainty of the selected values is  $\pm$  0.4 percent at 50 K, which decreases with increase in temperature to  $\pm 0.3$  percent at 300 K. Below 50 K, the uncertainty increases with decrease in temperature to  $\pm 1$  percent at 1 K. Published values of  $\gamma$  and  $\theta_D(0)$  are compared in figure 7; the values selected are  $\gamma = 6.55 \pm 0.05$  mJ/K<sup>2</sup> · mol and  $\theta = 235 \pm 1$  K.

TABLE 7.	Sources of heat-capacity data on iridium used in the analysis	

	Temperature	Purity of	Electronic	Debye	Entropy at 298.15 K			Experime	ntal method		
Year	measurements	Weight Percent	mJ/K <sup>2</sup> · mol × 10 <sup>3</sup>	temperature, θ at 0 K K	J/K · mol	cal/K · mol	Calorimeter design	Thermometer	Temperature scale	Cooling of sample	References
1931	273-1808	?					MM-Cu	TC(Cu-Cn)	TC(Pt-Rh)		[44, 45]
1933	289-1273	?					MM-Cu				[105]
1955	1.2-20	99,98	3140	420			VI-I	phosphor bronze, constantan	1948- <sup>4</sup> He, vp·H <sub>2</sub> gas	cond	[106]
1955	11–276	99.9	3510	$\theta_{ m 0}(10) = 430$	35.56	8.50	VI-I	РЬ	Pb, vp·H <sub>2</sub> , vp·O <sub>2</sub> , gas	gas	[15, 16]



FIGURE 6. Deviations of the heat-capacity data of the literature on iridium from the selected values in the range 0 to 300 K. The estimated limit of accuracy, the temperature derivative,  $dC_p/dT$ , in  $J/K^2$  mol, and the Debye characteristic temperature  $\theta_D(T)$  of the selected values. (The values of  $\theta_D(T)$  were calculated from the relations  $C_n = C_p - \gamma T$  and  $D(\theta/T) = C_n/3R$ . See text for further details.) For the  $\theta_D(T)$  the lines at 100 K and above correspond to 1 percent of the heat capacity and those below 100 K, 10 percent of the heat capacity.

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T V		$(H^{\circ}_{T} - H^{c}_{0})$	$(H_T^\circ - H_0^c)/T$	$(S_{\tau}^{\circ}-S_{0}^{c})$	$-(G_T^\circ - H_0^c)$	$-(G_T^\circ - H_0^c)/T$
	J/K · moi	J/moi	J/K · moi	J/K · mol	J/mol	J/K · mol
0.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.00000
1.00	.00323	.00161	.00161	.00321	.00160	.00160
2.00	.00661	.00650	.00325	.00647	.00643	.00322
3.00	.0103	.0149	.00498	.00984	.0146	.00486
4.00	.0145	.0273	.00682	.0134	.0262	.00654
5.00	.0193	.0441	.00882	.0171	0414	00827
6.00	.0249	.0661	.0110	.0211	0604	0101
7.00	.0314	.0941	.0134	0254	0836	0110
8.00	.0390	.129	.0161	0301	111	.0119
9.00	.0480	.173	.0192	.0352	.144	.0160
10.00	0587	296	0226	0407	100	0100
11.00	0716	.220	.0220	.0407	.182	.0182
12.00	.0710	.291	.0204	.0409	.220	.0205
12.00	107	.570	.0300	.0538	.270	.0230
14.00	130	.407	.0339	.0010	.334	.0257
14.00	.150	.303	.0410	.0703	.399	.0285
15.00	.159	.729	.0486	.0802	.475	.0316
16.00	.192	.904	.0565	.0915	.560	.0350
17.00	.232	1.115	.0656	.104	.658	.0387
18.00	.279	1.370	.0761	.119	.769	.0427
19.00	.334	1.675	.0882	.135	.896	.0472
20.00	.398	2.041	.102	.154	1.041	0520
25.00	.916	5.177	.207	.292	2 121	0848
30.00	1.804	11.83	.394	.532	4 132	138
35.00	2.972	23.68	677	895	7 648	210
40.00	4.333	41.87	1.047	1.379	13.28	.332
45.00	5.010					
45.00	5.813	67.21	1.494	1.974	21.62	.481
50.00	7.314	100.0	2.001	2.664	33.18	.664
55.00	8.759	140.3	2.550	3.430	48.39	.880
60.00	10.11	187.5	3.124	4.251	67.58	1.126
65.00	11.34	241.1	3.710	5.109	90.96	1.399
70.00	12.46	300.7	4.295	5.991	118.7	1.696
75.00	13.47	365.5	4.874	6.886	150.9	2.012
80.00	14.39	435.2	5,440	7,785	187.6	2.345
85.00	15.23	509.3	5.992	8.683	228.7	2.691
90.00	16.00	587.4	6.527	9.576	274.4	3.049
95.00	16 71	669.2	7 044	10.46	294 5	2 416
100.00	17.36	754.4	7 544	10.40	379.0	3.410
105.00	17.96	842 7	8.026	12.90	137.9	4.170
110.00	18.51	033.0	8 400	12.20	500.0	4.170
115.00	19.01	1028.	8.937	13.88	568.2	4.534
100.00	10.45					_
120.00	19.47	1124.	9.366	14.70	639.7	5.331
125.00	19.89	1222.	9,779	15.50	715.2	5.721
130.00	20.27	1323.	10.18	16.29	794.6	6.113
135.00	20.62	1425.	10.56	17.06	878.0	6.504
140.00	20.93	1529.	10.92	17.81	965.2	6.894
145.00	21.22	1634.	11.27	18.55	1056.	7.284
150.00	21.49	1741.	11.61	19.28	1151.	7.671
155.00	21.75	1849.	11.93	19.99	1249.	8.057
160.00	21.98	1958.	12.24	20.68	1351.	8.441
165.00	22.20	2069.	12.54	21.36	1456.	8.822
170 00	22 41	2180	19.83	99.03	1564	0.901
175.00	22.71	2100.	12.00	22.03	1676	9.201
180.00	22.00	2233.	10.10	22.00	1070.	9.5//
185.00	22.17	2400.	13.37	20.32	1/91.	9.950
100.00	22.70	2021.	13.03	23.95	1909.	10.32
120.00	20.10	2050.	15.87	24.50	2030.	10.09

 TABLE 8.
 Thermodynamic properties of Iridium solid phase, atomic weight = 192.2

T K	$\begin{array}{c} C_p \\ J/K \cdot mol \end{array}$	$(H_T^\circ - H_0^c)$ J/mol	$\frac{(H_{\tau}^{\circ} - H_{0}^{\circ})/T}{J/K \cdot mol}$	$\begin{array}{c} (S_{\tau}^{\circ} - S_{0}^{c}) \\ \mathbf{J/K \cdot mol} \end{array}$	$\begin{array}{c c} -(G_{\tau}^{\circ}-H_{0}^{c})\\ \text{J/mol} \end{array}$	$\frac{-(G_T^\circ - H_0^c)/T}{J/K \cdot mol}$
195.00	23.29	2752.	14.11	25.16	2155.	11.05
200.00	23.43	2869.	14.34	25.75	2282.	11.41
205.00	23.57	2986.	14.57	26.34	2412.	11.77
210.00	23.71	3105.	14.78	26.90	2545.	12.12
215.00	23.83	3224.	14.99	27.46	2681.	12.47
220.00	23.95	3343.	15.20	28.01	2820.	12.82
225.00	24.06	3463.	15.39	28.55	2961.	13.16
230.00	24.16	3584.	15.58	29.08	3105.	13.50
235.00	24.26	3705.	15.76	29.60	3252.	13.84
240.00	24.35	3826.	15.94	30.11	3401.	14.17
245.00	24.44	3948.	16.11	30.62	3553.	14.50
250.00	24.52	4070.	16.28	31.11	3708.	14.83
255.00	24.59	4193.	16.44	31.60	3864.	15.15
260.00	24.66	4316.	16.60	32.08	4024.	15.48
265.00	24.73	4440.	16.75	32.55	4185.	15.79
270.00	24.79	4564.	16.90	33.01	4349.	16.11
273.15	24.83	4642.	16.99	33.30	4454.	16.30
275.00	24.85	4688.	17.05	33.47	4515.	16.42
280.00	24.91	4812.	17.19	33.91	4684.	16.73
285.00	24.96	4937.	17.32	34.36	4854.	17.03
290.00	25.01	5062.	17.45	34.79	5027.	17.34
295.00	25.06	5187.	17.58	35.22	5202.	17.63
298.15	25.09	5266.	17.66	35.48	5314.	17.82
300.00	25.10	5312.	17.71	35.64	5379.	17.93

TABLE 8. Thermodynamic properties of Iridium solid phase, atomic weight = 192.2 - Continued

 $H_0^c$  and  $S_0^c$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

Some of the measurements were not considered in the analysis because of the uncertainty in the purity of sample, the relatively poor guality of the data, or the data being mean values over large temperature intervals. The relative-enthalpy measurements that have not been considered are also listed in this group. The data that have not been considered in the analysis are: Dulong and Petit [26] (mean values between 0 °C and 100 and 300 °C), Pouillet [72] (relative enthalpy between 0 °C and temperature up to 1600 °C), Byström [10] (mean values by the method of mixtures between 0 and 300 °C), Weinhold [100] (relative enthalpy between temperatures of 10 to 25 °C and temperatures up to 952 °C), Violle [96] (relative enthalpy between 0 °C and temperatures up to 1177 °C), Pionchon [70] (relative enthalpy between 0 °C and temperatures up to 1048 °C), Behn [3] (mean values by the method of mixtures between 18 °C and 100, -79, and -186 °C), Tilden [89. 90] (mean values by the method of mixtures between 0 to 15 °C at temperatures from -182 to 1177 °C), Gaede [30] (direct electrical measurements between 18 and 92 °C), Wigand [104] (mean values by the method of mixtures using Bunsen ice calorimeter between 0 °C and temperatures up to 162 °C), Schlett [81] (mean values by the method of mixtures using Bunsen ice calorimeter between 0 °C and temperatures up to 100 °C), Richards and Jackson [77] (mean values by the method of mixtures between 20 °C and -188 and 100 °C), Dewar [23] (mean values between the normal boiling points of nitrogen and hydrogen), Fabaro [28] (continuous heating method between 890 and 1543 °C), Roth and Chall [78] (mean values by the method of mixtures between 13 and 50 °C), Esser, Averdieck, and Grass [27] (relative enthalpy using copper block calorimeter between 0 °C and temperatures up to 1100 °C), and Kraftmakher and Lanina [53] (modulation of ac heating between 1000 and 2000 K).

The following are data that were analyzed: Simon and Zeidler [83] reported measurements from 18 to 208 K on a platinum wire sample. The calorimeter was one of the early vacuum-adiabatic design described by Lange [55]. The temperatures were determined using a Pb-resistance thermometer [79]. The data deviate from +2 to -7 percent from the selected values. Very little weight was given to their data. Simon and Zeidler [83] smoothed their data with the literature values [17] up to 300 K. Figures 8 and 9 show the deviation of their smoothed values from the selected values.

Barnes and Maass [2] reported enthalpy measurements relative to 298.15 K (25 °C) down to 195 K (-78 °C) on a pure platinum sample vessel to be used in other measurements. The method of mixtures was used with a gas-filled adiabatic water-bath calorimeter operated at about 298 K. Copper-constantan thermopile was used in controlling the adiabatic shield temperature relative to that of the calorimeter. A Beckman thermometer installed in the adiabatic shield was used to determine the change in the calorimeter temperature indirectly. The data deviate from 2 to -5 percent from the selected values. Very little weight was given to the data.

Kok and Keesom [52] reported measurements from 1.1 to 20.3 K on rolled sheets of platinum of 99.95 percent purity, the ratio of 4.2 K to ice point (0 °C) resistance of a wire drawn from the material being 0.01385. The sample was sealed in a copper vessel with helium exchange gas. An isothermal-jacket vacuum calorimeter was used. Phosphor-bronze and constantan wire thermometers were employed in the ranges 1 to 6 K and 6 to 20 K, respectively. The resistance thermometers were calibrated against the vapor pressures of helium and hydrogen and a gas thermometer. The data deviate as much as 13 percent (mostly above  $\pm 2$  percent) from the selected values; they are not plotted. Very little weight was given to the data.

Persoz [65, 66, 63] reported measurements at 11 temperatures between 308 and 1254 K using a unique vacuum-adiabatic calorimeter. 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. Persoz [65, 66, 63] gave no information on the purity of the platinum sample he used. The data around 300 K are about 2 percent lower than the selected values. Very little weight was given to the data.

Kurrelmeyer, Mais, and Green [54] reported measurements between -78 and 100 °C obtained by pulse heating in which a capacitor was discharged through a wire sample in a bridge circuit. The heat capacity was calculated from the circuit resistances, the initial charge on the capacitor, and the change in resistance  $\Delta R$  of the platinum wire sample and its R(T) calibration. The data are about 1 to 2 percent higher than the selected value. Very little weight was given to the data.

Rayne [74] reported measurements from 0.2 to 1 K on two specimens of platinum, one of two percent impurity content and the other 99.99 percent pure. (See the section on palladium for the description of the method.) The lattice contribution was considered negligible and the electronic coefficients reported. The low purity sample yielded an abnormally high

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 $\gamma$  (174.4 mJ/K<sup>2</sup> · mol); the pure sample yielded

$$\gamma = 6.90 \pm 0.33 \text{ mJ/K}^2 \cdot \text{mol}$$

Recently, Shoemake and Rayne [82] reported measurements between 1.4 and 100 K on a sample of 99.999 percent purity. A "calibrated" germanium thermometer was employed. No reference is given to the temperature scale used. A mechanical heat switch was used in cooling the sample. The authors fitted the observed data below 4.2 K to an equation of the form

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

The values  $\gamma = 6.56 \pm 0.03 \text{ mJ/K}^2 \cdot \text{mol}$ ,  $\theta = 234.4 \pm 2.5 \text{ K}$ , and  $B = 1.8 \pm 2 \times 10^{-4} \text{ mJ/K}^6 \cdot \text{mol}$  are the only numerical data reported. The values of heat capacity based on these data are within about 1 percent of the selected values.

Strittmater and Danielson [86, 87] reported measurements between 338 and 727 K (65 and 454 °C) on a platinum wire sample of "thermometric" purity. A pulse heating method was used in which the sample in the form of 0.005 in. diameter wire was heated directly by an electric pulse of 0.055-s duration from ambient to 727 K. The heat capacity was calculated from the high-speed observations of the current and voltage drop across a known section of the platinum wire. The same current and voltage observations served in the determination of the wire temperature as a function of time. The data in the region above 300 K are 2 to 3 percent lower than the expected values. Very little weight was given to the data in selecting the best values in the region of 300 K.

Butler and Inn [9] reported measurements between 337 and 1164 K. The specific heat was determined from the time-temperature observations of a specimen electrolytically coated with platinum black thermally radiating to a blackened isothermal enclosure. A chromel-alumel thermocouple was employed in the determination of the temperatures. The data in the region above 300 K are about 11 percent lower than the expected values. No weight was given to the data.

Clusius, Losa, and Franzosini [17] reported measurements between 11 and 274 K on a platinum sample of 99.94 percent purity, with 0.01 and 0.03 percent of Pd and Rh, respectively, as impurities. A trace amount of Fe and between trace and limit of detectibility of Ag, Cu. Ca, and Mg were present. The measurements were made in an isothermal jacket vacuum calorimeter. The temperatures were determined by means of a Pb-resistance thermometer calibrated against the vapor pressures of oxygen and hydrogen [20, 79]. The data on the average are within about  $\pm 0.2$  percent of the selected values.

Ramanathan and Srinivasan [73] reported measurements between 1.2 and 4.2 K on a platinum sample of 99.99 percent purity. An isothermal jacket vacuum

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

and obtained  $\gamma = 6.676 \text{ mJ/K}^2 \cdot \text{mol}$  and  $\theta_D(0) = 239.7 \text{ K}$ . The values of heat capacity based on these values of  $\gamma$  and  $\theta_D(0)$  are about 1 percent higher than the selected values at 1 K and in close agreement at 4 K.

Budworth, Hoare, and Preston [7] reported measurements between 1.8 and 4.2 K on a "spectroscopically standardized" sample of platinum in which the "individual impurities were of the order of 2 or 3 ppm." The carbon resistance thermometer employed was calibrated in terms of the 1955L-<sup>4</sup>He vapor-pressure scale [92, 93]. Budworth et al. considered the accuracy of the data insufficient for recalculation on the basis of the 1958-<sup>4</sup>He scale [6]. The electronic coefficient of heat capacity  $\gamma$  reported is 6.41 ±0.026 mJ/K<sup>2</sup> · mol and the  $\theta_D(0)$  reported is 235.3 ±1.3 K. The data are about 2 percent lower than the selected values.

Dixon, Hoare, Holden, and Moody [25] reported measurements on a sample of platinum of 99.99 purity containing as impurities: Pd, 0.007 percent, Rh and Fe, 0.001 percent, and Ag and Cu 0.001 percent. The material was chill cast into a graphite mold and swaged to approximate size in several stages with intervening anneals at 850 °C and cold water guenches. The sample was boiled in dilute hydrochloric acid and finally annealed in vacuum. The measurements were made between 1.2 and 4.2 K using a mechanical heat switch in cooling the sample. Temperatures were determined by means of carbon resistance thermometers calibrated in terms of the 1958-4He vapor-pressure scale [6]. The observations were fitted by means of the least squares method to obtain the coefficients of the equations:  $C = \gamma T + AT^3$  and  $C = \gamma T + AT^3 + DT^{3/2}$ , where the coefficients  $\gamma$  and A have their usual significance. The coefficient D corresponds to the spin-wave contribution to the heat capacity. The values of  $\gamma$  and  $\theta_D(0)$  obtained by fitting the first equation were  $6.507 \pm 0.006$ mJ deg<sup>-2</sup> mol<sup>-1</sup> and 234.9  $\pm 0.4$  K, respectively. The values of  $\gamma$ ,  $\theta_D(0)$ , and D obtained by fitting to the second equation were  $6.568 \pm 0.074 \text{ mJ/K}^2 \cdot \text{mol.}$ 233.4  $\pm$  1.7 K, and -0.051  $\pm$  0.062 mJ/K<sup>5/2</sup> · mol, respectively. The values of heat capacity based on these parameters deviate about -0.5 percent from the selected values

Dixon, Hoare, and Holden [24] reported measurements from 1.2 to 4.2 K on the platinum specimen used earlier by Budworth, Hoare, and Preston [7]. The material was chill cast from the melt. Temperatures were determined by means of a carbon-resistance thermometer calibrated in terms of the 1958-<sup>4</sup>He vaporpressure scale [6]. A mechanical heat switch was used in cooling the sample. The data were fitted by means of the least squares method to two equations of the form:  $C = \gamma T + AT^3$  and  $C = \gamma T + AT^3 + BT^5$ , obtaining, respectively, the electronic coefficients of the heat capacity 6.507  $\pm 0.007$  and 6.517  $\pm 0.012$  mJ/K<sup>2</sup> · mol, the values of  $\theta_D(0)$  234.9  $\pm 0.8$  and 235.5  $\pm 1.6$  K, and  $B = 0.17 \pm 0.20 \times 10^{-2}$  mJ/K<sup>6</sup> · mol. The values of  $\gamma$  and  $\theta_D(0)$  from the equation  $C = \gamma T + AT^3$  are identical to those reported earlier in the paper by Dixon, Hoare, Holden, and Moody [25]; probably the same data were reported.

Tsiovkin and Vol'kenshteyn [91] reported measurements between 1.6 and 8 K on a sample of 99.99 percent purity. A carbon resistance thermometer was used. The temperature scale is not given. The electronic coefficient of heat capacity,  $\gamma = 7 \text{ mJ/K}^2 \cdot \text{mol}$ , only is reported. The value is somewhat higher than the selected value.

Andres and Jensen [1] list  $\gamma = 6.54 \text{ mJ/K}^2 \cdot \text{mol}$  and  $\theta_D(0) = 213 \text{ K}$  as private communication from J. P. Maita. The data are almost as much as 8 percent higher than the selected values.

Berg [4] reported measurements between 2.6 and 20 K on zone-refined rods of 0.25 in. diameter and 1 in. length. The results of spectrochemical analysis showed the sample to be about 99.99 percent pure. The rods were vacuum annealed at 1000 °C for 24 hours prior to the measurements. A carbon resistance thermometer was used, calibrated in terms of the 1958-<sup>4</sup>He vapor-pressure scale [6], helium gas thermometer, and NBS-1955 scale [34, 62]. Berg fitted by the method of least squares the data between 2.6 and 7 K to an equation of the form

$$\dot{C} = \gamma T + AT^3 + BT^5,$$

from which were obtained:

$$\gamma = 6.59 \pm 0.3 \text{ mJ/K}^2 \cdot \text{mol},$$
  
 $\theta_D(0) = 240.1 \pm 2.3 \text{ K},$   
 $B = 2.3 \pm 1.5 \times 10^{-4} \text{ mJ/K}^6 \cdot \text{mol}.$ 

The values of heat capacity based on these parameters are within about  $\pm 0.7$  percent of the selected values. The observed values of heat capacity between 7 and 20 K are within  $\pm 0.2$  percent of the selected values.

The following data above 300 K served to help select the best values in the region of 300 K: White [103] reported relative enthalpy measurements between 20 and 1300 °C. The values around 300 K are 0.5 to 0.7 percent lower than his earlier preliminary measurements [101, 102]. The heat capacity at 300 K derived from the relative enthalpy data is 2 percent higher than the selected value.

Wüst, Meuthen, and Durrer [107] reported relative enthalpy measurements between 0 and 1500 °C. A Bunsen ice calorimeter was employed. The data are about 0.5 percent lower than the selected values in the region of 300 K.

	Temperature	Purity of	Electronic	Debye	Entropy a	at 298.15 K		Experime	ntal method		_
Year	measurements K	Weight Percent	heat capacity, $\gamma$ mJ/K <sup>2</sup> · mol × 10 <sup>3</sup>	temperature, θ at 0 K K	J/K · mol	cal <u>/</u> K · mol	Calorimeter design	Thermometer	Temperature scale	Cooling of sample	Reference
1909	273-1773	?		······································			MM-water				[101, 10
1918	273-1773	?					MM-water				[103]
1918	273-1773	?					MM-ice				[107]
1926	18-208	"Heraeus"		225			VA–I	Рь	Рь	gas	[83]
1928	273-1877	?					MM-Cu	TC(Cu-Cn)	TC(Pt-Rh)		[40, 41,
1930	195-298	?					MM-water	Hg	ITS	gas	[2]
1932	273-1664	?					MM-Cu	TC(Cu−Cn)	TC(Pt-Rh)		[47, 48]
1936	1.1-20	99.95	6724	233			VI-I	phosphor- bronze, constantan	vp-4He, vp-H <sub>2</sub> gas	gas	[52]
1954	0.2-1	99,99	6900 ± 330 °				VI–I	MS	MS. 1948–4He gas	AD-MC	[74]
1957	11-274	99,94	6611	$\theta_D(20) = 221$	41.63±0.08"	$9.95 \pm 0.02^{a}$	VI–I	Рь	Pb, vp-H2 vp-O2	gas	[17]
1959	1.2-4.2	99.99	6676±42°	239.7			VI–I	с	1955L⁴He	MHS	[73]
1960	1.8-4.2	"spectro- scopically standardized"	6410±26°	235.3±1.3 <sup>b</sup>			VI-I	С	1955L⁴He	cond	[7]

a on platinum used in the analysis TABLE 9 Sol urges of he 

1962	299-1079	99.99				MM-DE				[51]
1965	1.2-4.2	99.99	$6507 \pm 6^{b}$ $6568 \pm 74^{b.c}$	234.9±0.4 <sup>b</sup> 233.4±1.7 <sup>b,c</sup>		VI-I	С	1958–4He	MHS	[25]
1965	1.6-8	99.99	7000			VI-I	с	?	MHS	[91]
1967	1.2-4.2	"spectro- scopically standarcized" chill cast	6507 ± 7 <sup>b</sup> 6517 ± 12 <sup>b,d</sup>	234.9±0.8 <sup>b</sup> 236.5±1.6 <sup>b,d</sup>		VI-I	C .	1958⁴He	MHS	[24]
1968	1.4-100	99,999	$6560 \pm 30^{b,d}$	$234.4 \pm 2.5^{b,d}$		?	Ge	?	MHS	[82]
1969	26-20	99,99	6590 ± 30 <sup>5,4</sup>	240.1±2.3 <sup>b, d</sup>		VA-I	с	1958-4He gas, NBS-1955	LC	[4]
1969	300-1900	99.9948				СН	TC(Pt-Rh)	TC(Pt-Rh)		[99]

<sup>a</sup>Figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the estimated uncertainties in the values given.

<sup>b</sup>Figures prefixed with the ± symbols have been interpreted from the authors' description to indicate the precision of the values given.

From the equation of the form:

 $C = \gamma T + AT^3 + DT^{3/2}$ , where

 $A = (12\pi^4 R/5) \ [\theta_D(0)]^{-3}$ 

<sup>d</sup>From the equation of the form:

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



FIGURE 7. Comparison of the reported values of electronic coefficients of heat capacity,  $\gamma$ , and Debye characteristic temperatures,  $\theta_D(0)$ , of platinum. The figures (without decimal) along the horizontal lines indicate literature references in section 5.



FIGURE 8. Deviations of the heat-capacity data of the literature on platinum from the selected values in the range 30 to 300 K and the estimated limit of accuracy. The temperature derivative,  $dC_p/dT$ , in J/K<sup>2</sup> mol and the Debye characteristic temperature  $\theta_D(T)$  of the selected values. (The values of  $\theta_D(T)$  were calculated from the relations  $C_v = C_p - \gamma T$  and  $D(\theta/T) = C_v/3R$ . See text for further details.) For the  $\theta_D(T)$  the vertical lines at 100 K and above correspond to 1 percent of the heat capacity and those below 100 K, 10 percent of the heat capacity.

Jaeger and Rosenbohm [40, 41, 46, 37] and Jaeger, Rosenbohm, and Bottema [47, 48] reported measurements on platinum of "Heraeus' purest quality" by the method of mixtures between 0° and 1625 °C. The data around 300 K are within 0.2 percent of the selected values.

Kendall, Orr, and Hultgren [51] reported four different series of relative enthalpy measurements between 298 and 1435 K, the platinum samples investigated being in the form of (1) a solid sphere, (2) a hollow sphere (sample vessel) of the same size made from the foil sample that was used to fill it, and the hollow sphere filled with (3) the foil and with (4) a wire sample. The three sets of results obtained from the data are in good agreement (0.2 or 0.3 percent) with the earlier work of Jaeger and colleagues [40, 41, 46, 47, 48, 37] and of White [101, 102, 103]. The data are within 0.3 percent of the selected values in the region of 300 K.

Vollmer and Kohlhaas [99] reported measurements between 300 and 1900 K on a sample of 99.9948 percent purity employing a continuous heating method. At 300 K the reported value is almost 7 percent lower than the selected value. No weight was given to the data.

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FIGURE 9. Deviations of the heat-capacity data of the literature on platinum from the selected values in the range 0 to 30 K.

TABLE 10. Thermodynamic properties of Platinum solid phase, atomic weight=195.09

T K	$\begin{array}{c} C_p \\ \mathbf{J/K} \cdot \mathbf{mol} \end{array}$	$(H_T^\circ - H_0^c)$ J/mol	$(H_T^\circ - H_0^c)/T$ J/K · mol	$  (S_T^\circ - S_0^c)  J/K \cdot mol$	$\begin{array}{c} -(G_T^\circ - H_0^c) \\ J/mol \end{array}$	$\begin{vmatrix} -(G_T^\circ - H_0^c)/\\ J/K \cdot mol \end{vmatrix}$
0.00	0.000000	0.000000	0.00000	0.000000	0.000000	0.00000
1.00	00670	0.000000	00331	00660	00320	0.00000
2.00	0142	0127	.00531	0135	0122	.00329
2.00	.0145	.0137	.00005	.0155	.0155	.00005
3.00	.0237	.0325	.0108	.0210	.0305	.0102
4.00	.0358	.0620	.0155	.0294	.0556	.0139
5.00	.0515	.105	.0211	.0390	.0897	.0179
6.00	.0720	.167	.0278	.0501	.134	.0223
7.00	0986	251	0359	0631	191	0272
8.00	199	266	0458	0784	261	0276
9.00	.175	.519	.0577	.0964	.348	.0387
NA 60			,			
10.00	.228	.720	.0720	.118	.455	.0455
11.00	.293	.980	.0891	.142	.584	.0531
12.00	.370	1.311	.109	.171	.741	.0617
13.00	.461	1.725	.133	.204	.928	.0714
14.00	.566	2.238	.160	.242	1.150	.0822
15.00	.687	2.863	.191	.285	1.414	.0942
16.00	825	3,618	226	334	1 799	108
17.00	070	4 510		200	9,009	100
10.00	1,150	4.510	.200	.300	2.005	.125
19.00	1.150	5.581	.310	.449	2.501	.139
19.00	1.550	0.824	.335	.310	2.903	.157
20.00	1.542	8.262	.413	.590	3.536	.177
25.00	2.776	18.92	.757	1.060	7.590	.304
30.00	4.287	36.48	1.216	1.697	14.42	.481
35.00	5,939	62.02	1.772	2.481	. 24.80	709
40.00	7.609	95.90	2.398	3.383	39.42	.985
45.00	0.000	100.0		1		
45.00	9.223	138.0	3.067	4.373	58.78	1.306
50.00	10.73	187.9	3.759	5.424	83.25	1.665
55.00	12.11	245.1	4.456	6.512	113.1	2.056
60.00	13.34	308.8	5.146	7.620	148.4	2.473
65.00	14.44	378.3	5.820	8.732	189.3	2.912
70-00	15 43	453.0	6 471	0.830	935 7	3 367
75.00	16.21	522 4	7.009	10.02	200.7	0.007
10.00	10.51	552.4	7.090	10.95	201.1	3.835
AU.UU 07.00	17.10	n15.9	7.699	12.01	345.0	4.313
85.00	17.81	703.2	8.2/3	13.07	407.7	4.797
90.00	18.40	793.9	8.821	14.11	475.7	5.285
95.00	19.03	887.7	9.344	15.12	548.8	5.777
100.00	19.55	984.1	9.841	16.11	626.9	6.269
105.00	20,02	1083.	10.31	17.08	709.8	6.760
110.00	20.46	1184.	10.77	18.02	797.6	7 251
115.00	20.85	1288.	11.20	18.93	890.0	7.739
190.00		1202		10.05	004.5	
120.00	21.22	1393.	11.01	19.83	986.9	8.224
125.00	21.55	1500.	12.00	20.70	1088.	8.706
130.00	21.86	1608.	12.37	21.55	1194.	9.184
135.00	22.14	1718.	12.73	22.38	1304.	9.657
140.00	22.40	1830.	13.07	23.20	1418.	10.13
145.00	22 64	1949	13 30	22.00	1536	10 50
150.00	22.07	7056	13.37	20.99	1000.	10.09
100.00	22.00	2030.	10.71	29.10	1030.	11.05
122.00	23.07	21/1.	14.01	25.51	1783.	11.50
160.00	23.26	2287.	14.29	26.25	1913.	11.95
165.00	23.43	2403.	14.57	26.96	2046.	12.40
170.00	23.60	2521.	14.83	27.67	2182.	12 84
175.00	23.75	2630	15.09	20.01	0200	12.04
100.00	20.10	2039.	15.00	20.33	2322.	13.2/
100.00	23.89	2/58.	15.32	29.02	2400.	13.70
185.00	24.03	2878.	15.56	29.68	2612.	14.12
	1 14 14	90880	15 79	4 20 20	9769	1 34 54

<u>Т</u> К	$C_p$ I/K · mol	$(H_{T}^{\circ} - H_{0}^{c})$ $U mol$	$\frac{(H_T^\circ - H_0^c)}{1/K \cdot mol}$	$(S_T^\circ - S_0^c)$	$-(G_T^\circ - H_0^c)$	$\frac{-(G_T^\circ - H_0^c)/T}{1/K \cdot mol}$
	5/11		5/11 1101			
195.00	24.28	3120.	16.00	30.95	2916.	14.95
200.00	24.40	3242.	16.21	31.57	3072.	15.36
205.00	24.51	3364.	16.41	32.17	3231.	15.76
210.00	- 24.61	3487.	16.60	32.76	3394.	16.16
215.00	24.71	3610.	16.79	33.34	3559.	16.55
220.00	24.81	3734.	16.97	33.91	3727.	16.94
225.00	24.90	3858.	17.15	34.47	3898.	17.32
230.00	24.99	3983.	17.32	35.02	4072.	17.70
235.00	25.07	4108.	17.48	35.56	4248.	18.08
240.00	25.15	4233.	17.64	36.09	4427.	18.45
245.00	25.23	4359.	17.79	36.61	4609.	18.81
250.00	25.31	4486.	17.94	37.12	4793.	19.17
255.00	25.38	4612.	18.09	37.62	4980.	19.53
260.00	25.45	4740.	18.23	38.11	5170.	19.88
265.00	25.52	4867.	18.37	38.60	5361.	20.23
			]			
270.00	25.59	4995.	18.50	39.08	5555.	20.58
273.15	25.63	5075.	18.58	39.37	5679.	20.79
275.00	25.65	5123.	18.63	39.55	5752.	20.92
280.00	25.71	5251.	18.75	40.01	5951.	21.25
285.00	25.77	5380.	18.88	40.46	6152.	21.59
290.00	25.83	5509.	19.00	40.91	6356.	21.92
295.00	25.89	5638.	19.11	41.35	6561.	22.24
298.15	25.92	5720.	19.18	41.63	6692.	22.44
300.00	25.94	5768.	19.23	41.79	6769.	22.56
	I		1		I	

TABLE 10. Thermodynamic properties of Platinum solid phase, atomic weight=195.09-Continued

 $H_0^c$  and  $S_0^c$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

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# 6. Appendix A

.T	C <sub>n</sub>	$(H_m^\circ - H_n^\varepsilon)$	$(H^{\circ}_{r}-H^{\circ}_{s})/T$	$(S_n^\circ - S_n^\circ)$	$-(G_{-}^{\circ}-H^{\circ})$	$-(G^{\circ}-H^{\circ})/T$
K	cal/K · mol	cal/mol	cal/K mol	cal/K · mol	cal/mol	$cal/K \cdot mol$
0.00	0.000000	0.000000	0.000000	0.000000	0.00000	0.00000
1.00	.000708	.000353	.000353	.000706	.000353	.00035
2.00	.00144	.00142	.000711	.00142	.00141	.00070
3.00	.00220	.00324	.00108	.00214	.00319	.00106
4.00	.00302	.00584	.00146	.00289	.00571	.00143
5.00	.00392	.00930	.00186	.00366	.00898	.00180
6.00	.00490	.0137	.00228	.00446	.0130	.00217
7.00	.00601	.0191	.00274	.00529	.0179	.00256
8.00	.00724	.0258	.00322	.00617	.0236	.00295
9.00	.00862	.0337	.00374	.00710	.0303	.00336
10.00	.0102	.0431	.00431	.00809	.0379	.00379
11.00	.0119	.0541	.00492	.00914	.0465	.00422
12.00	.0139	.0670	.00558	.0103	.0562	.00468
13.00	.0161	.0820	.00631	.0115	.0670	.00516
14.00	.0186	.0993	.00709	.0127	.0791	.00565
						,
15.00	.0215	.119	.00796	.0141	.0925	.00617
16.00	.0247	.142	.00890	.0156	.107	.00671
17.00	.0283	.169	.00993	.0172	.124	.00728
18.00	.0324		.0111	.0189	.142	.00788
19.00	.0371	.234	.0123	.0208	.162	.00851
20.00	.0424	.274	.0137	.0229	.184	.00918
25.00	.0840	.578	.0231	.0363	.329	.0132
30.00	.162	1.174	.0391	.0578	560	0187
35.00	.283	2.268	.0648	.0913	927	0265
40.00	.449	4.081	.102	139	1 497	0374
45.00	.652	6.819	.152	.204	2.348	0522
50.00	.883	10.65	.213	.284	3.561	0712
55.00	1.133	15.68	.285	.380	5 215	0048
60.00	1.394	21.99	.367	490	7 384	192
65.00	1.656	29.62	.456	.612	10.13	156
					10.10	.150
70.00	1.915	38.55	.551	744	13 52	103
75.00	2.164	48.75	.650	.884	17.58	.175
80.00	2.402	60.17	.752	1.032	22.37	280
85.00	2.628	72.76	.856	1.184	27.91	328
90.00	2.841	86.43	960	1 341	34.99	380
					01.22	.000
95.00	3.041	101 1	1.065	1.500	41 39	495
100.00	3.229	116.8	1 168	1.660	40.92	.400
105.00	3.404	133.4	1.100	1.892	57.03	550
110.00	3.567	150.8	1.271	1.022	67.44	.002
115.00	3.718	169 1	1.371	2 146	77 77	.015
		107.1	1.710	2.140		.070
120.00	3.860	188.0	1 567	2 309	99.01	741
125.00	3,991	207.6	1.307	2.300	100.0	. 741
130.00	4 114	201.0	1.001	2.400	100.0	.807
135.00	4 228	227.9	1.735	2.027	115.0	.8/4
140.00	4 334	240.0	1.045	2.704	127.1	.942
170.00	7.004	210.2	1.930	2.940	141.4	1.010
145 00	4 432	202.1	2.014	2.004	156.5	1.070
150.00	4.400	292.1	2.014	3.094	156.5	1.079
100.00	4.525	514.5	2.097	3.246	172.4	1.149
155.00	4.010	337.3	2.176	3.395	189.0	1.219
100.00	4.590	360.6	2.254	3.543	206.3	1.289
105.00	4.703	384.2	2.329	3.689	224.4	1.360
170.00	4.000	100 5				
170.00	4.832	408.2	2.401	3.832	243.2	1.431
175.00	4.895	432.5	2.472	3.973	262.7	1.501
180.00	4.955	457.2	2.540	4.112	282.9	1.572

Thermodynamic properties of Ruthenium solid phase, atomic weight=101.07

### FURUKAWA, REILLY, AND GALLAGHER

### 6. Appendix A-Continued

T	<i>C</i> <sub>p</sub>	$(H_T^\circ - H_0^c)$	$(H_{\tau}^{\circ} - H_{0}^{c})/T$	$(S_T^\circ - S_0^c)$	$-(G_T^\circ - H_0^c)$	$-(G_T^\circ - H_0^c)/T$
K	cal/K · mol	cal/mol	$cal/K \cdot mol$	cal/K · mol	cal/mol	$cal/K \cdot mol$
185.00	.5.012	482.1	2.606	4.248	303.8	1.642
190.00	5.065	507.3	2.670	4.382	325.4	1.713
105 00					· · · · ·	
195.00	5.116	532.7	2.732	4.515	347.6	1.783
200.00	5.165	558.4	2.792	4.645	370.5	1.853
205.00	5.211	584.4	2.851	4.773	394.1	1.922
210.00	5.256	610.5	2.907	4.899	418.3	1.992
215.00	5.299	636.9	2.962	5.023	443.1	2.061
990.00	E 940	669 5	2.017	5.346	10.5	0.100
220.00	5.340	003.5	3.010	5.140	408.5	2.129
225.00	5.380	690.3	3.068	5.266	494.5	2.198
230.00	5.417	717.3	3.119	5.385	521.1	2.266
235.00	5.453	744.5	3.168	5.502	548.4	2.333
240.00	5.488	771.8	3.216	5.617	576.2	2.401
245.00	5.520	799 4	3 263	5 730	604 5	2 467
250.00	5.550	827.0	3 308	5 842	633 5	2.534
255.00	5.579	854.9	3 352	5.952	662.9	2.600
260.00	5 605	882.8	3 395	6.061	693.0	2.665
265.00	5 630	010.0	3 437	6 168	792 5	2.000
200.00	0.000	510.5	0.401	0.100	123.5	2.150
270.00	5.652	939.1	3.478	6.273	754.7	2.795
273.15	5.666	956.9	3.503	6.339	774.5	2.835
275.00	5.673	967.4	3.518	6.377	786.3	2.859
280.00	5.693	995.9	3.557	6.480	818.4	2.923
285.00	5.710	1024.	3.594	6.580	851.1	2.986
290.00	5.726	1053.	3.631	6.680	884.2	3.049
295.00	5.741	1082.	3.667	6.778	917.9	3.111
298.15	5.750	1100.	3.688	6.839	939.3	3.150
300.00	5.755	1110.	3.701	6.875	952.0	3.173
		1			1	1

Thermodynamic properties of Ruthenium solid phase, atomic weight = 101.07

 $H_{\delta}$  and  $S_{\delta}$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

# 7. Appendix B

Thermodynamic properties of Rhodium solid phase, atomic weight=102.905

T K	$C_p$ cal/K · mol	$(H^{\circ}_{T}H^{c}_{0})$ cal/mol	$(H_r^\circ - H_0^\circ)/T$ cal/K · mol	$(S_T^\circ - S_0^\circ)$ cal/K · mol	$-(G_{T}^{\circ}-H_{0}^{c})$ cal/mol	$-(G_{\tau}^{c}-H_{0}^{c})/T$ cal/K · mol
0.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.00000
1.00	.00111	.000557	.000557	.00111	.000556	.00055
2.00	.00225	.00224	.00112	.00223	.00223	.00111
3.00	.00343	.00507	.00169	.00337	.00502	.00167
4.00	.00467	.00911	.00228	.00452	.00896	.00224
5.00	.00599	.0144	.00289	.00570	.0141	.00281
6.00	.00742	.0211	.00352	.00692	.0204	.00340
7.00	.00900	.0293	.00419	.00818	.0279	.00399
8.00	.0108	.0392	.00490	.00949	.0368	.00459
9.00	.0127	.0509	.00566	.0109	.0469	.00521
10.00	.0150	.0648	.00648	.0123	.0585	.00585
11.00	.0176	.0811	.00737	.0139	.0716	.00651
12.00	.0206	.100	.00835	.0155	.0863	.00719
13.00	.0241	.122	.00942	.0173	.103	.00790
14.00	.0280	.148	.0106	.0192	.121	.00864
15.00	.0325	.179	.0119	.0213	.141	.00942
16.00	.0377	.214	.0134	.0236	.164	.0102

## 7. Appendix B-Continued

T	С.,	$(H^{\circ}_{-} - H^{\circ})$	$(H^{\circ}_{-}-H^{\circ}_{-})/T$	$(S^{\circ}_{-} - S^{\circ}_{-})$	$-(G^{\circ}_{-}-H^{\circ})$	$-(G^{\circ}_{-}-H^{\circ}_{-})/T$
ĸ	cal/K · mol	cal/mol	cal/K · mol	$cal/K \cdot mol$	cal/mol	$cal/K \cdot mol$
17.00	.0438	.254	.0150	.0261	.189	.0111
18.00	.0507	.302	.0168	.0287	.216	.0120
19.00	.0586	.356	.0187	.0317	.246	.0130
20.00	.0678	.419	.0210	.0349	279	0140
25.00	138	014	0366	0567	504	0909
20.00	.150	1 007	.0500	.0007	.304	.0202
50.00	.201	1.007	.0029	.0919	.809	.0290
35.00	.434	3.603	.103	.144	1.452	.0415
40.00	.655	6.305	.158	.216	2.345	.0586
45.00	.918	10.22	.227	.308	3.648	.0811
50.00	1.205	15.53	.311	.420	5.461	.109
55.00	1.497	22.28	.405	.548	7.874	143
60.00	1 784	30.49	508	601	10.07	192
45.00	2.061	40.11	.500	.071	10.97	.105
05.00	2.001	40:11	.017	.645	14.80	.228
70.00	2.326	51.08	.730	1.007	19.43	.278
75.00	2.577	63.34	.845	1.176	24.89	.332
80.00	2.813	76.82	.960	1.350	31.20	.390
85.00	3.035	91.45	1.076	1.528	38.39	.452
90.00	3.241	107.1	1.190	1.707	46.48	516
95.00	3 434	123.8	1 304	1 887	55.46	584
100.00	3 612	141 5	1.004	2.069	65.95	.504
100.00	2 777	141.0	1.410	2.000	03.33	.034
105.00	3.777	159.9	1.523	2.248	70.14	.725
110.00	3.930	179.2	1.629	2.428	87.84	.799
115.00	4.071	199.2	1.732	2.605	100.4	.873
120.00	4.201	219.9	1.832	2.782	113.9	.949
125.00	4.322	241.2	1.930	2.956	128.2	1.026
130.00	4.435	263.1	2.024	3.127	143.4	1,103
135.00	4.539	285.5	2,115	3 297	159.5	1 181
140.00	4 635	308.5	2 203	3 463	176 4	1.101
		000.0	2.205	0.400	110.4	1.200
145.00	4 795	221.0	9 900	2 400	104.1	1 200
150.00	4.120	255.7	2.209	3.020	194.1	1.339
150.00	4.009	555.7	2.371	3.789	212.7	1.418
155.00	4.887	380.0	2.451	3.948	232.0	1.497
160.00	4.960	404.6	2.529	4.105	252.2	1.576
165.00	5.028	429.6	2.603	4.258	273.1	1.655
170.00	5.092	454.9	2.676	4.409	294.7	1.734
175.00	5.152	480.5	2.746	4.558	317.1	1.812
180.00	5.209	506.4	2.813	4.704	340.3	1 801
185.00	5 263	532.6	2 879	4 847	364.9	1.051
190.00	5 313	550.0	2.019	4.099	200.0	1.709
170.00	0.010	000.0	2.742	4.700	300.0	2.040
105.00	5 961	505 7	2 004	5 105		
195.00	5.301	585.7	3.004	5.127	414.1	2.123
200.00	5.407	612.6	3.063	5.263	440.0	2.200
205.00	5.450	639.8	3.121	5.397	466.7	2.277
210.00	5.491	667.1	3.177	5.529	494.0	2.352
215.00	5.530	694.7	3.231	5.659	522.0	2.428
			}			
220,00	5.567	722.4	3.284	5.786	550.6	2 503
225.00	5.602	750.3	3 335	5 912	579.8	2.000
230.00	5 636	778.4	2 284	6.025	600.7	2.311
005 00	5.000	004 7	0.004	0.055	009.7	2.051
200.00	5.008	000.7	3.433	0.157	640.2	2.724
240.00	5.698	835.1	3.480	6.277	671.3	2.797
045 00	5 501	060.5	0.505			
245.00	5.726	863.7	3.525	6.394	702.9	2.869
250.00	5.753	892.4	3.569	6.510	735.2	2.941
255.00	5.779	921.2	3.612	6.624	768.0	3.012
260.00	5.803	950.1	3.654	6.737	801.5	3.083
265.00	5.826	979.2	3.695	6.848	835.4	3 153
	,					0.100

Thermodynamic properties of Rhodium solid phase, atomic weight = 102.905

### FURUKAWA, REILLY, AND GALLAGHER

### 7. Appendix B-Continued

			-	·	0	
 T K	$C_p$ cal/K · mol	$(H_T^\circ - H_0^c)$ cal/mol	$\frac{(H_T^\circ - H_0^\circ)/T}{\mathrm{cal/K} \cdot \mathrm{mol}}$	$(S_{\tau}^{\circ} - S_{0}^{\circ})$ cal/K · mol	$-(G_{T}^{\circ}-H_{0}^{c})$ cal/mol	$-\frac{(G_{\tau}^{\circ}-H_{0}^{\circ})/T}{\operatorname{cal/K}\cdot\operatorname{mol}}$
 270.00	5.848	1008.	3.735	6.957	869.9	3.222
273.15	5.861	1027.	3.759	7.025	891.9	3.265
275.00	5.869	1038.	3.773	7.064	905.0	3.291
280.00	5.888	1067.	3.811	7.170	940.6	3.359
285.00	5.907	1097.	3.848	7.275	976.7	3.427
290.00	5.925	1126.	3.883	7.377	1013.	3.494
295.00	5.941	1156.	3.918	7.479	1050.	3.561
298.15	5.952	1175.	3.939	7.542	1074.	3.603
300.00	5.957	1186.	3.952	7.579	1088.	3.627
		1	1		1	1

Thermodynamic properties of Rhodium solid phase, atomic weight = 102.905

 $H_o^c$  and  $S_o^c$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

## 8. Appendix C

Thermodynamic properties of Palladium solid phase atomic weight = 106.4

 T.	$C_{p}$	$(H^{\circ}_{\pi} - H^{c}_{\circ})$	$(H_T^\circ - H_0^c)/T$	$(S_r^\circ - S_0^c)$	$-(G_{\tau}^{\circ}-H_{0}^{c})$	$-(G_T^c-H_0^c)/T$
K	cal/K · mol	cal/mol	cal/K · mol	cal/K · mol	cal/mol	cal/K · mol
 0.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.00000
1.00	.00227	.00113	.00113	.00225	.00113	.00113
 2.00	.00467	.00458	.00229	.00455	.00452	.00226
3.00	.00735	.0106	.00352	.00694	.0103	.00342
4.00	.0104	.0194	.00485	.00947	.0185	.00461
5.00	.0140	.0316	.00632	.0122	.0293	.00585
6.00	.0183	.0477	.00795	.0151	.0429	.00714
7.00	.0234	.0685	.00979	.0183	.0595	.00850
8.00	.0296	.0949	.0119	.0218	.0796	.00994
9.00	.0370	.128	.0142	.0257	.103	.0115
10.00	.0458	.169	.0169	.0300	.131	.0131
11.00	.0564	.220	.0200	.0349	.164	.0149
12.00	.0688	.283	.0236	.0403	.201	.0168
13.00	.0833	.359	.2076	.0464	.244	.0188
14.00	.0997	.450	.0321	.0531	.294	.0210
15.00	.118	.559	.0372	.0606	.351	.0234
16.00	.139	.687	.0429	.0689	.416	.0260
17.00	.162	.837	.0492	.0780	.489	.0288
18.00	.186	1.011	.0562	.0879	.572	.0318
19.00	.214	1.211	.0637	.0987	.665	.0350
20.00	942	1 430	0710	110	770	0385
25.00	428	3.001	194	183	1 494	0598
20.00	673	5 821	194	282	2 647	0882
35.00	965	0.021		407	4 360	125
40.00	1 285	15 59	388	557	6 762	169
40.00	1.200	1.1.12		.001	0.102	.107
45.00	1.616	22.77	.506	.727	9.965	.221
50.00	1.945	31.68	.634	.915	14.06	.281
55.00	2.263	42.20	.767	1.115	19.14	.348
60.00	2.564	54.28	.905	1.325	25.23	.421
65.00	2.843	67.80	1.043	1.542	32.40	.498
			-			
70.00	3.102	82.67	1.181	1.762	40.65	.581
75.00	3.339	98.78	1.317	1.984	50.02	.667
80.00	3.556	116.0	1.450	2.207	60.60	.756
85.00	3.755	134.3	1.580	2.428	72.08	.848
90.00	3.937	153.6	1.706	2.648	84.77	.942

## 8. Appendix C-Continued

T	C.,	$(H_{\pi}^{\circ}-H_{\pi}^{\circ})$	$(H^{\circ}_{-}-H^{\circ}_{-})/T$	$(S^{\circ}_{-} - S^{\circ}_{-})$	$-(G^{\circ}_{-}-H^{\circ}_{-})$	$-(G^{\circ}_{-}-H^{\circ}_{-})/T$
v	cal/K mol	cal/mol	$cal/K \cdot mol$	$cal/K \cdot mol$	cal/mol	$cal/K \cdot mol$
		·cai/moi				
95.00	4.105	173.7	1.828	2.865	98.56	1.037
100.00	4.259	194.6	1.946	3.080	113.4	1.134
105.00	4.400	216.2	2.059	3.291	129.4	1.232
110.00	4.581	238.6	2.169	3.499	146.3	1.330
115.00	4.652	261.5	2.274	3.703	164.3	1.429
120.00	4.764	285.1	2.376	3.904	183.4	1.528
125.00	4.867	309.1	2.473	4.100	203.4	1.627
130.00	4.962	333.7	2.567	4.293	224.4	1.726
135.00	5.050	358.8	2.657	4.482	246.3	1.824
140.00	5.131	384.2	2.744	4.667	269.2	1.923
145.00	5.206	410.1	2.828	4.848	293.0	2.020
150.00	5.275	436.3	2.908	5.026	317.6	2.118
155.00	5.340	462.8	2.986	5.200	343.2	2.214
160.00	5.400	489.7	3.060	5.371	369.6	2.310
165.00	5.456	516.8	3.132	5.538	396.9	2.405
170.00	5.508	544.2	3.201	5.701	425.0	2.500
175.00	5.557	571.9	3.268	5.862	453.9	2.594
180.00	5.603	599.8	3.332	6.019	483.6	2.687
185.00	5.647	627.9	3.394	6.173	514.1	2.779
190.00	5.688	656.2	3.454	6.324	545.3	2.870
195.00	5.726	684.8	3.512	6.472	577.3	2.961
200.00	5.763	713.5	3.567	6.618	610.1	3.050
205.00	5.797	742.4	3.621	6.760	643.5	3.139
210.00	5.830	771.5	3.674	6.901	677.7	3.227
215.00	5.861	800.7	3.724	7.038	712.5	3.314
220.00	5.890	830.1	3.773	7.173	748.0	3.400
225.00	5.918	859.6	3.820	7.306	784.2	3.485
230.00	5.944	889.2	3.866	7.436	821.1	3.570
235.00	5.968	919.0	3.911	7.564	858.6	3.654
240.00	5.991	948.9	3.954	7.690	896.7	3.736
	6.030	0.50 0				
245.00	6.013	978.9	3.996	7.814	935.5	3.818
250.00	0.034	1009.	4.030	7.930	974.9	3.899
255.00	0.054	1039.	4.076	8.055	1015.	3.980
260.00	0.073	1070.	4.114	8.173	1055.	4.059
265.00	6.090	1100.	4.151	8.289	1097.	4.138
070.00	6 107	1100	4 707	0.400	1100	1.024
270.00	6.107	1130.	4.187	8.403	1138.	4.216
273.13	0.117	1150.	4.209	0.4/4	1105.	4.205
2/3.00	0.123	1101.	4.222	8.515	1181.	4.293
200.00	0.130	1172.	4.200	0.020	1223.	4.309
285.00	0.155	1222.	4.289	8.134	1207.	4.445
000.00	6.167	1052	4 200	0.040	1911	4.500
290.00	0.107	1200.	4.322	0.042	1311.	4.520
220.00	6 198	1204.	4.000	0.747	1200.	4.074
250.10	6 102	1315	4.312	9.013	1304.	4.040
900.00	0.170	1010.	4.000	9.001	1400.	4.000

Thermodynamic properties of Palladium solid phase atomic weight = 106.4

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 $H^c_0$  and  $S^c_0$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

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## 9. Appendix D

T	$C_{\mu}$	$(H_{\pi}^{\circ}-H_{0}^{c})$	$(H_r^\circ - H_r^c)/T$	$(S_r^{\circ} - S_r^c)$	$-(G_r^{\circ}-H_{\circ}^c)$	$-(G_r^{\circ}-H_c^{\circ})/T$
К	cal/K · mol	cal/mol	cal/K · mol	cal/K · mol	cal/mol	cal/K · mol
0.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
1.00	.000771	.000384	.000384	.000767	.000383	.00038
2.00	.00158	.00155	.000777	.00155	.00154	.00076
3.00	.00246	.00357	.00119	.00235	.00348	.00116
4.00	.00346	00652	00163	00319	00625	00156
1.00		.00002	.00100	.00017	.00020	.00100
5.00	00461	0105	00211	00409	00080	00108
5.00	00504	.0105	00211	.00403	.00909	.00190
0.00	.00394	.0136	.00203	.00504	.0144	.00241
7.00	.00749	.0225	.00321	.00607	.0200	.00286
8.00	.00931	.0309	.00386	.00719	.0266	.00333
9.00	.0115	.0412	.00458	.00840	.0344	.00382
10.00	0140	0510	00500	00074	0495	00405
11.00	0171	.0339	.00539	.00974	.0435	.00435
11.00	.0171	.0095	.00031	.0112	.0539	.00490
12.00	.0209	.0884	.00737	.0129	.0659	.00550
13.00	.0255	.112	.00858	.0147	.0797	.00613
14.00	.0311	.140	.00998	.0168	.0955	.00682
	-					
15.00	.0379	.174	.0116	.0192	.113	.00756
16.00	.0459	.216	.0135	.0219	.134	.00837
17.00	.0554	.267	.0157	.0249	.157	.00925
18.00	.0666	.327	.0182	.0284	.184	.0102
19.00	0798	400	0211	0324	214	0113
17.00	.0150	.400	.0211	.0324	.217	.0115
20.00	.0952	.488	.0244	.0368	.249	.0124
25.00	219	1 237	0495	0698	507	0203
30.00	421	2 9 9 9	.0425	197	099	0200
30.00	.401	2.020	.0940	.127	1,000	.0329
35.00	./10	5.059	.102	.214	1.828	.0522
40.00	1.036	10.01	.250	.330	3.175	.0794
45 00	1 389	16.06	357	479	5 168	115
50.00	1.009	22.01	179	627	7 021	150
50.00	1.740	25.91	.4/0	.037	1.931	.139
55.00	2.094	33.52	.609	.820	11.57	.210
60.00	2.416	44.81	.747	1.016	16.15	.269
65.00	2.710	57.63	.887	1.221	21.74	.334
70.00	0.070	73.04	1.005	1 490	00.07	105
70.00	2.978	/1.80	1.027	1.432	28.37	.405
75.00	3.220	87.37	1.165	1.646	36.07	.481
80.00	3.440	104.0	1.300	1.861	44.83	.560
85.00	3.640	121.7	1.432	2.075	54.67	.643
90.00	3.824	140.4	1.560	2.289	65.58	.729
95.00	3.993	159.9	1.684	2.500	77.55	.816
100.00	4.149	180.3	1.803	2.709	90.58	.906
105.00	4.292	201.4	1.918	2.915	104.6	.997
110.00	4.424	223.2	2.029	3.118	119.7	1.088
115.00	4.544	245.6	2.136	3.317	135.8	1.181
		· · ·				
120.00	4.654	268.6	2.239	3.513	152.9	1.274
125.00	4.753	292.1	2.337	3.705	170.9	1.367
130.00	4.844	316.1	2.432	3.893	189.9	1.461
135.00	4.927	340.6	2.523	4.077	209.8	1.554
140.00	5.003	365.4	2.610	4.258	230.7	1.648
145.00	5.073	390.6	2.694	4.435	252.4	1.741
150.00	5.137	416.1	2.774	4.608	275.0	1.834
155.00	5,197	442.0	2.851	4.777	298.5	1.926
160.00	5 252	468 1	2.001	4 943	322.8	2 017
147 00	5.200	404.5	2.920	5 104	247.0	2.017
102.00	5.500	474.0	2.991	9.100	041.7	2.109
170.00	5.355	521 1	3 066	5.265	373.8	2,199
175.00	5 402	548 0	3 132	5 421	400.6	2.289
100.00	5 116	575 9	2 105	5 579	198.0	9 278
100.00	0.440	313.4	9.139	0.010	420.0	1 2.070

Thermodynamic properties of Iridium solid phase, atomic weight=192.2

### 9. Appendix D-Continued

ī	C	$(H^\circ - H^\circ)$	$(H^\circ - H^\circ)/T$	$(S^{\circ}-S^{\circ})$	$-(G^\circ - H^\circ)$	$-(G^{\circ}-H^{\circ})/T$
K	$cal/K \cdot mol$	cal/mol	$cal/K \cdot mol$	$cal/K \cdot mol$	cal/mol	al/K · mol
105 00	E 400	602 5	2 957	5 792	456.3	2 466
185.00	5.488	602.5	5.257	5.725	430.3	2.400
190.00	5.528	030.0	3.310	5.870	403.3	2.004
195.00	5.565	657.8	3.373	6.014	515.0	2.641
200.00	5 601	685.7	3.428	6.156	545.4	2.727
205.00	5 634	713.8	3.482	6.294	576.5	2.812
210.00	5.666	742.0	3 534	6 430	608.3	2.897
210.00	5 606	770 4	3 583	6 564	640.8	2 981
215.00	0.000	110.7	0.000	0.001		
220.00	5.724	799.0	3.632	6.695	674.0	3.064
225.00	5.750	827.7	3.679	6.824	707.8	3.146
230.00	5,775	856.5	3.724	6.951	742.2	3.227
235.00	5.798	885.4	3.768	7.075	777.3	3.308
240.00	5.820	914.5	3.810	7.198	813.0	3.387
	,					
245.00	5.840	943.6	3.851	7.318	849.3	3.466
250.00	5.859	972.9	3.891	7.436	886.1	3.545
255.00	5.878	1002.	3.930	7.552	923.6	3.622
260.00	5.895	1032.	3.968	7.667	961.7	3.699
265.00	5.911	1061.	4.004	7.779	1000.	3.775
270.00	5.926	1091.	4.040	7.890	1039.	3.850
273.15	5.935	1109.	4.062	7.958	1064.	3.897
275.00	5.940	1120.	4.074	7.998	1079.	3.924
280.00	5.953	1150.	4.108	8.106	1119.	3.998
285.00	5.966	1180.	4.140	8.211	1160.	4.071
290.00	5.978	1210.	4.172	8.315	1202.	4.143
295.00	5.989	1240.	4.202	8.417	1243.	4.215
298.15	5.996	1259.	4.221	8.481	1270.	4.260
300.00	6.000	1270.	4.232	8.518	1286.	4.286
	1					L

Thermodynamic properties of Iridium solid phase, atomic weight = 192.2

 $H^c_0$  and  $S^c_0$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.

### 10. Appendix E

Thermodynamic properties of Platinum solid phase, atomic weight=195.09

T K	$C_p$ cal/K · mol	$(H_T^\circ - H_0^c)$ cal/mol	$(H_{T}^{\circ}-H_{0}^{c})/T$ cal/K · mol	$(S_{\tau}^{\circ} - S_{0}^{c})$ cal/K · mol	$-(G_{\tau}^{\circ}-H_{0}^{c})$ cal/mol	$\frac{-(G_{T}^{\circ}-H_{0}^{\circ})/T}{\operatorname{cal}/\mathbf{K}\cdot\operatorname{mol}}$
0.00	0.000000	0.000000	0.000000	0.000000	0.000000	0.00000
1.00	.00160	.000792	.000792	.00158	.000786	.00078
2.00	.00342	.00327	.00164	.00323	.00318	.00159
3.00	.00566	.00777	.00259	.00502	.00729	.00243
4.00	.00855	.0148	.00370	.00702	.0133	.00332
5.00	.0123	.0252	.00503	.00932	.0214	.00429
6.00	.0172	.0398	.00664	.0120	.0320	.00534
7.00	.0236	.0601	.00858	.0151	.0455	.00651
8.00	.0317	.0875	.0109	.0187	.0624	.00780
9.00	.0419	.124	.0138	.0230	.0832	.00925
10.00	.0546	.172	.0172	.0281	.109	.0109
11.00	.0700	.234	.0213	.0340	.140	.0127
12.00	.0885	.313	.0261	.0409	.177	.0148
13.00	.110	.412	.0317	.0488	.222	.0171
14.00	.135	.535	.0382	.0578	.275	.0196
15.00	164	(04	0456	0(0)	000	0005
15.00	.104	.684	.0456	.0681	.338	.0225
16.00	.197	.865	.0540	.0798	.412	.0257

# FURUKAWA, REILLY, AND GALLAGHER

# 10. Appendix E-Continued

T	hermodynamic	properties o	f Platinum	solid	phase,	atomic	weight =	195.09

Т	$C_p$	$(H^{\circ}_{T} - H^{c}_{0})$	$(H_r^\circ - H_s^\circ)/T$	$(S_r^\circ - S_r^\circ)$	$-(G_r^\circ - H_{\varsigma})$	$-(G_m^\circ - H_s^\circ)/T$
К	cal/K · mol	cal/mol	cal/K · mol	cal/K · mol	cal/mol	cal/K · mol
17.00	234	1 090	0625	0099	400	0000
18.00	275	1 334	.0055	.0928	.498	.0293
19.00	320	1.631	0858	.107	.390	.0332
17100	.020	1.001	.0050	.125	.715	.0375
20.00	.368	1.975	0987	141	845	0493
25.00	.663	4 521	181	253	1 814	.0423
30.00	1.025	8 720	.101	.200	2.445	.0720
35.00	1 419	14.82	.291	502	5.440	.115
40.00	1.819	22 92 92	573	800	0.920	.109
					2.441	.230
45.00	2.204	32.99	.733	1 045	14.05	319
50.00	2.565	44.92	.898	1.296	19.90	308
55.00	2.893	58.58	1.065	1.556	27.03	.491
60.00	3.188	73.80	1.230	1.821	35.47	.591
65.00	3.452	90.41	1.391	2.087	45.24	.696
70.00	3.687	108.3	1.547	2.352	56.34	805
75.00	3.898	127.2	1.697	2.613	68.75	.917
80.00	4.087	147.2	1.840	2.871	82.46	1.031
85.00	4.257	168.1	1.977	3.124	97.45	1 146
90.00	4.410	189.8	2.108	3.372	113.7	1.263
						1.200
95.00	4.548	212.2	2.233	3.614	131.2	1.381
100.00	4.672	235.2	2.352	3.850	149.8	1.498
105.00	4.786	258.9	2.465	4.081	169.7	1.616
110.00	4.889	283.0	2.573	4.306	190.6	1.733
115.00	4.984	307.7	2.676	4.526	212.7	1.850
120.00	5.071	332.9	2.774	4.740	235.9	1.966
125.00	5.151	358.4	2.867	4.948	260.1	2.081
130.00	5.225	384.4	2.957	5.152	285.3	2.195
135.00	5.292	410.7	3.042	5.350	311.6	2.308
140.00	5.355	437.3	3.123	5.544	338.8	2.420
145.00	5.412	464.2	3.201	5.733	367.0	2.531
150.00	5.464	491.4	3.276	5.917	396.2	2.641
155.00	5.513	518.8	3.347	6.097	426.2	2.750
160.00	5.558	546.5	3.416	6.273	457.1	2.857
165.00	5.600	574.4	3.481	6.444	488.9	2.963
170.00	5.640	602.5	3.544	6.612	521.6	3.068
175.00	5.676	630.8	3.605	6.776	555.0	3.172
180.00	5.711	659.3	3.663	6.937	589.3	3.274
185.00	5.743	687.9	3.718	7.094	624.4	3.375
190.00	5.774	716.7	3.772	7.247	660.2	3.475
195.00	5.803	745.7	3.824	7.398	696.9	3.574
200.00	5.831	774.7	3.874	7.545	734.2	3.671
205.00	5.857	804.0	3.922	7.689	772.3	3.767
210.00	5.882	833.3	3.968	7.831	811.1	3.862
215.00	5.906	862.8	4.013	7.969	850.6	3.956
000.00	F 000	0000 1				
220.00	5.929	892.4	4.056	8.105	890.8	4.049
225.00	5.951	922.1	4.098	8.239	931.6	4.141
230.00	5.972	951.9	4.139	8.370	973.2	4.231
235.00	5.993	981.8	4.178	8.498	1015.	4.321
240.00	6.012	1012.	4.216	8.625	1058.	4.409
945 00	6 021	1049	4.059	0.710	1100	
243.00	0.031	1042.	4.253	8.749	1102.	4.490
250.00	0.049	1072.	4.288	8.871	1146.	4.583
200,00	0.00/	1102.	4.323	8.991	1190.	4.668
200.00	0.084	1133.	4.357	9.109	1236.	4.752
205.00	0.100	1163.	4.390	9.225	1281.	4.835

## 10. Appendix E-Continued

$-(G_T^\circ - H_0^c)/T$
cai/K · mol
4.918
4.969
4.999
5.080
5.159
5.238
5.316
5.364
5.393
-

Thermodynamic properties of Platinum solid phase, atomic weight = 195.09

 $H_0^c$  and  $S_0^c$  apply to the reference state of the solid at zero K and 1 atmosphere pressure.