

A Critical Evaluation of the Thermophysical Properties of Mercury

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For the use of a mercury column for precise pressure measurements — such as the pressurized 30 meter mercury-in-steel column used at the Van der Waals-Zeeman Laboratory for the calibration of piston gauges up to nearly 300 MPa — it is highly important to have accurate knowledge of such properties of mercury as density, isobaric secant and tangent volume thermal expansion coefficients, and isothermal secant and tangent compressibilities as functions of temperature and pressure. In this paper we present a critical assessment of the available information on these properties. Recommended values are given for the properties mentioned and, in addition, for properties derived from these such as entropy, enthalpy, internal energy, and the specific heat capacities.

Key words: compressibility; density; mercury; thermal expansion; thermodynamic properties.

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1. Introduction

For the use of mercury as an accurate pressure exerting medium, accurate knowledge of its density is essential. Absolute determinations of the density of mercury at atmospheric pressure have been made by several authors. Well-known are the experiments of Cook and Stone,¹ and Cook.² Two methods have been used: the displacement method and the content method. The displacement method¹ involves the hydrostatic weighing of a hard metal cube plunged into mercury. In the content method² the density is calculated from the mass of mercury filling a hollow cube. Also one *relative* (to water) content density determination has been reported.³ Relative determinations of the density of mercury have been obtained by comparing samples of mercury with a reference sample, applying the displacement method⁴. As a fundamental reference value we use in this paper the density of mercury at 293.150 K (ITS-48) and at 1 standard atmosphere as stated by Cook.² The correction of the density, at the same temperature and pressure, to ITS-90 is -0.030 kg/m^3 . Secant coefficients of volume thermal expansion in the range 273–623 K at atmospheric pressure have been measured by Beattie *et al.*⁵ The isothermal tangent compressibility at atmospheric pressure in the temperature range 273–343 K was measured by Hubbard and Loomis.⁶ The pressure dependence of density—the isothermal compressibility—can be determined either statically or dynamically. The static method, direct measurement of volume change by pressure, is the one applied by Bridgman (1911)⁷ and Hayward.⁸ Here, accurate determination of the isothermal compressibility is very important: at higher pressures most of the error in the density is due to the error in the compressibility. The dynamic method, used by Davis and Gordon,⁹ is based on measurements of the velocity of sound as a function of temperature and pressure. From these data and known values of density ρ_0^T , isobaric tangent volume thermal expansion coefficient α , and isobaric specific heat capacity $C_{p,0}^T$ as functions of temperature at atmospheric pressure, the values of ρ_p^T , α , and $C_{p,p}^T$ at higher pressures are derived by stepwise integration using thermodynamic equations for $(\partial\rho/\partial p)_T$, $(\partial\alpha/\partial p)_T$, and $(\partial C_p/\partial p)_T$. Davis and Gordon⁹ used this method for determining the density of mercury at three temperatures and pressures up to 1.3 GPa. We corrected the density values of Davis and Gordon by comparing their isothermal secant bulk modulus at a certain temperature and pressure with a highly accurate secant bulk modulus at the same temperature and pressure measured by Hayward.⁸

The values of the density of mercury at 293.150 K and one standard atmosphere reported in the literature are evaluated. We consider the possible effects of impurities and refer to the influence of changes in the abundances of isotopes with respect to the density. We mention our purification method and a simple but highly effective criterion for the purity of mer-

cury. The density of mercury in the temperature range 293–323 K and the pressure range 0–300 MPa is calculated. A double polynomial equation for the density of mercury is applied to calculate thermodynamic properties, which can be considered as recommended values. These values are compared with experimental values reported by Bridgman (1911),⁷ Bett, Weale, and Newitt,¹⁰ Stallard, Rosenbaum, and Davis, Jr.,¹¹ and Grindley and Lind, Jr.,¹² with values stated in a review monograph by Vukalovich *et al.*¹³ and with theoretical values calculated by Kumari and Dass.¹⁴

2. Density of Mercury

2.1. Introduction

The volume V_p^T and density ρ_p^T of mercury at a temperature T and at an applied pressure p can be represented by

$$V_p^T = V_0^T (1 + \bar{\alpha} (T - T_0))(1 - \bar{\kappa} p) \quad (1)$$

and

$$\rho_p^T = \rho_0^T / (1 + \bar{\alpha} (T - T_0))(1 - \bar{\kappa} p) \quad (2)$$

where:

the temperatures T and $T_0 = 273.15$ are expressed in K, and the applied pressure p in MPa,

$\bar{\alpha}$ is the isobaric secant volume thermal expansion coefficient, which is in general for applied pressure p defined as

$$\bar{\alpha} = \text{secant } \alpha_p^T \equiv \frac{(V_p^T - V_p^{T_0})}{V_p^{T_0}(T - T_0)} = \frac{(\rho_p^{T_0} - \rho_p^T)}{\rho_p^T(T - T_0)} \quad (3)$$

$\bar{\kappa}$ is the isothermal secant compressibility coefficient, i.e.

$$\bar{\kappa} = \text{secant } \kappa_p^T \equiv \frac{(V_0^T - V_p^T) / (V_0^T p)}{(\rho_p^T - \rho_0^T) / (\rho_p^T p)} \quad (4)$$

At atmospheric pressure, thus when the applied or gauge pressure is zero, Eqs. (1) and (2) are written:

$$V_0^T = V_0^{T_0} (1 + \bar{\alpha} (T - T_0)) \quad (5)$$

and

$$\rho_0^T = \rho_0^{T_0} / (1 + \bar{\alpha} (T - T_0)) \quad (6)$$

where:

$$\bar{\alpha} = \text{secant } \alpha_0^T$$

All temperatures in this paper are expressed in terms of K on ITS-90, unless stated otherwise. For the transformation of temperature values from ITS-27 into ITS-48, from IPTS-48 into IPTS-68 and from IPTS-68 into ITS-90, we consulted respectively the papers of Corruccini,¹⁵ Barber,¹⁶ and Preston-Thomas.¹⁷ As was the case for the IPTS-48 with respect to ITS-48, the amended Edition of 1975 of the IPTS-68 introduced no numerical changes.¹⁷

2.2. Reference Density at 293.150 K

Cook and Stone¹ and Cook² have reported two complementary absolute measurements of the density of mercury at 293.150 K (IPTS-48) and at 1 standard atmosphere. In the first paper the density of mercury was measured by a method consisting of two weighings. In the first weighing the mass of a hard metal cube of *known volume* is determined. In the second weighing the *apparent* mass of this cube immersed in mercury is determined. This method is called the displacement method. In the second paper the density of mercury was calculated from the mass of mercury filling a hollow cube formed of optically worked blocks of fused silica with known internal dimensions, which could be measured by optical interference. This pycnometer procedure is called the content method. Cook's experimental paper² contains also a survey and evaluation of his experimental results, using both methods.^{1,2} As mean density, at 293.150 K and one standard atmosphere is found:

$$\rho_0^{293.150} = 13545.854 \text{ kg/m}^3 \quad (7)$$

with a standard deviation of 0.003 kg/m³. Cook² states that there is a high probability that the density of any sample of pure mercury will be within 0.015 kg/m³ of this value. The value quoted above is obtained upon conversion from 293.150 K on IPTS-48 to 293.150 K on ITS-90. The conversion of the value of the density at 293.150 K from IPTS-48 into ITS-90 is taken from Ambrose¹⁸; the conversion from IPTS-48 into IPTS-68 from Chattle.¹⁹ Our corresponding value at 293.150 K on IPTS-68 is the same as in the more detailed Table of Chattle¹⁹ (range 273.15–313.15 K) and in the Table of Ambrose (1976)²⁰ (range 253.15–573.15 K), both derived from the same sources: Cook² and Beattie *et al.*⁵ This value is also adopted by the Comité International des Poids et Mesures (CIPM) (Barber¹⁶) and by the State Committee for Standards at the Board of Ministers of the Soviet Union (Adametz²¹).

In Table 1 we present the *mean* values of one relative and six absolute density determinations of mercury.^{3,1,2,22,23,21,24} In this table we also mention the method applied, the relative uncertainty, and, for the investigators^{23,21,24} of the Physikalisch-Technische Bundesanstalt (PTB), the number of samples to differentiate the *mean* value found by each author. Remarkable is the excellent agreement in mean value between the measurements of Fürtig²³ and the three more recent measurements of Adametz and Wloka.²⁴

Kuzmenkov²² claims the use of a fundamentally new absolute method for the determination of the density of mercury. A cube of known volume and mass is put in a pycnometer, which is additionally filled with mercury. The pycnometer is weighed when filled with the cube and mercury, and when filled with mercury alone. We consider this method as a hybrid of the two methods mentioned above.

Long-term stability of the density of mercury is very important. Patterson and Prowse²⁵ made a study of two pairs of mercury samples (not mentioned in Table 1), which both have been compared over a long period with the Australian reference sample NSL, measured by Cook.² The origin or source,

the method of cleaning, and the storage conditions of all the mercury samples used in this investigation are extensively reported (Patterson and Prowse²⁵). The first comparison extended over four years and the second over twenty-eight years. Patterson and Prowse state that both separate pairs of mercury samples failed to show a statistically significant change in density during long-term storage. Of course, it is possible that two samples of a comparison pair changed by about equal amounts in the same direction but, according to the authors, this is unlikely, due to differences in preparation and storage conditions.

From Table 1 we note that the differences of the density values with respect to the reference value of Cook² vary from -0.05 kg/m^3 to $+0.03 \text{ kg/m}^3$. The differences are larger than the uncertainty of 0.015 kg/m^3 estimated by Cook.² Due to the influence of chemical impurities and variation in isotopic content on the density of mercury,¹ it is necessary for accurate work, where the relative density needs to be known to better than a few times 10^{-6} , that the density is measured *absolutely* (e.g. Cook²) or *relatively* by comparing the sample to be measured with a sample that was earlier measured absolutely (e.g. Patterson and Prowse⁴).^{1,23,4}

In our 30 m mercury column we use mercury that has been thoroughly purified by a process developed by Michels.²⁶ In the first phase of this process tiny droplets of mercury drift slowly down in long tubes containing, successively, petroleum ether, a solution of $\text{Hg}(\text{NO}_3)_2$, and a 15 percent solution of HNO_3 . By this procedure most of the amount of base metals (such as Zn, Cd, Pb, and Cu) is dissolved. In the second phase the mercury is distilled four times at a low pressure of a few torr. Metals more noble than mercury (such as Ag, Au, and Pt) remain in the still while the yet remaining base metals are oxidized. Oxides of base metals are "deadening" the surface of mercury; appearance and mobility of mercury are changed. Surface behaviour of mercury is an extremely sensitive criterion of its purity; impurities in concentrations of 0.1 ppm can be easily recognized as discussed by Wichers²⁷ and Gordon and Wichers.²⁸ Two analytical atomic spectrometric methods were applied to examine our mercury. First an emission method (d.c. arc) was used for a qualitative analysis. All elements were found to be below the *detection* limit. The second method was an absorption method; it uses a graphite-furnace atomic-absorption spectrometer (GFAAS) for a quantitative analysis. All important metals turned out to be below the *determination* limit, so the investigation was confined to a semi-quantitative one. The results in ppb (parts per billion) are presented in Table 2.

The amounts of impurities mentioned in Table 2 are, according to Cook and Stone,¹ less than that which might produce a change of 0.014 kg/m^3 or relatively 1×10^{-6} in the density of mercury. The density of our mercury has been determined by CSIRO, Division of Applied Physics, Sydney, Australia. This determination, carried out by Patterson and Prowse⁴, has been based on a *relative displacement method*, where the unknown density is compared with the density of a reference sample, i.e. the NSL sample of Cook.² It was found that the density of our mercury at 293.150 K and one standard atmosphere is 0.002 kg/m^3 or 0.15×10^{-6} lower than the value of Cook² as mentioned in Table 1.

2.3. Isobaric Thermal Expansion

Cook²⁹ reviewed the published data on the isobaric secant volume thermal expansion coefficient of mercury and concluded that the equation given by Beattie *et al.*⁵ is the most reliable of the published formulations. This equation for the isobaric secant volume thermal expansion coefficient $\bar{\alpha}$, is only valid at atmospheric pressure (applied or gauge pressure is zero); we refer to Eqs. (5) and (6). The data of Beattie *et al.*⁵ have been refitted by Ambrose¹⁸ for temperatures in °C on ITS-90; we transformed his equation for temperatures in K on ITS-90:

$$\bar{\alpha} = 182.3887 \times 10^{-6} - 1.01689 \times 10^{-8} T + 2.2231 \times 10^{-11} T^2 + 1.5558 \times 10^{-14} T^3 \quad (8)$$

where:

$$T \text{ is in K and } \bar{\alpha} \text{ is in K}^{-1},$$

the range of the temperature is 253–573 K.

We calculated the standard deviation of $\bar{\alpha}$ out of 9 measurements from Beattie *et al.*⁵ as $0.008 \times 10^{-6} \text{ K}^{-1}$. Applying Eqs. (6) and (8) and the value for $\rho_0^{293.150}$ (7) one obtains

$$\rho_0^{273.150} = 13595.08 \text{ kg/m}^3. \quad (9)$$

Ambrose¹⁸ estimated that the errors in the density are likely to be within 0.02 kg/m^3 in the temperature range 273 K to 283 K and 303 K to 323 K, and within 0.01 kg/m^3 over the range 283 K to 303 K. Outside these ranges the probable error strongly increases.¹⁸

Four versions of the isobaric volume thermal expansion coefficient may be defined; here they are indicated by α_1 , α_2 , α_3 , and α_4 . Though we never read a paper in which α_2 was used, we discuss it here for theoretical reasons. Unfortunately the use of α_2 is a real possibility. The coefficients α_1 and α_2 are secant α 's; the coefficients α_3 and α_4 are tangent α 's.

1. The coefficient α_1

The coefficient α_1 is identical to the isobaric secant volume thermal expansion coefficient $\bar{\alpha}$, defined by Eq. (3). In analogy to Eq. (8) for atmospheric pressure, one can write, in general,

$$\alpha_1 = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \quad (10)$$

where:

$$T \text{ is in K}$$

with pressure dependent coefficients a_0 through a_3 , so that

$$V_p^T = V_p^{T_0} (1 + \alpha_1 (T - T_0)) \quad (11)$$

where:

absolute temperature $T_0 = 273.15 \text{ K}$.

2. The coefficient α_2

The coefficient α_2 is also a secant α , which is defined as,

$$\alpha_2 \equiv (V_p^T - V_p^{T_0}) / V_p^T (T - T_0) \quad (12)$$

so that

$$\alpha_2 = \alpha_1 / (1 + \alpha_1 (T - T_0)) \quad (13)$$

3. The coefficient α_3

The coefficient α_3 is a tangent α , which is defined as,

$$\alpha_3 \equiv (1 / V_p^{T_0})(\partial V_p^T / \partial T)_p \quad (14)$$

so that

$$\alpha_3 = \partial(\alpha_1 (T - T_0)) / \partial T)_p \quad (15)$$

or,

$$\alpha_3 = \alpha_1 + (T - T_0)(\partial \alpha_1 / \partial T)_p. \quad (16)$$

4. The coefficient α_4

The coefficient α_4 is identical to the isobaric tangent volume thermal expansion coefficient α as used in this paper. Because

$$\alpha_4 = \alpha = \text{tangent } \alpha_p^T \equiv (1 / V_p^T)(\partial V_p^T / \partial T)_p \\ = - (1 / \rho_p^T)(\partial \rho_p^T / \partial T)_p \quad (17)$$

so that

$$\alpha_4 = \alpha_3 / (1 + \alpha_1 (T - T_0)). \quad (18)$$

From Eqs. (10), (13), (16), and (18) we conclude that at an applied pressure p and $T = T_0 = 273.15$ K

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4. \quad (19)$$

From the definitions for α_1 , α_2 , α_3 and α_4 it is evident that the secant α_1 and the tangent α_3 are increasing functions of the temperature, while in our temperature range of 293–323 K the secant α_2 and the tangent α_4 are decreasing functions of the temperature. This behavior can also be deduced from Table 3, where the results of the four isobaric volume thermal expansion coefficients are given for the temperatures that Davis and Gordon⁹ used in their measurements.

The coefficient α_1 is used by Beattie *et al.*⁵ and Ambrose¹⁸; α_3 by Beattie *et al.*,⁵ and α_4 by Davis and Gordon⁹ and in theoretical studies. The possible use of these four different isobaric volume thermal expansion coefficients may lead to confusion. Therefore, we strongly advocate to use only the secant α_1 and the tangent α_4 , in this paper usually called $\bar{\alpha}$ and α , respectively.

2.4. Isothermal Compressibility

In analogy with the isobaric volume thermal expansion coefficients α_1 , α_2 , α_3 , and α_4 we define isothermal compressibility coefficients κ_1 , κ_2 , κ_3 , and κ_4 and their reciprocals, the isothermal bulk moduli K_1 , K_2 , K_3 and K_4 . The coefficients κ_1 , κ_2 and the moduli K_1 and K_2 are secant quantities; the coefficients κ_3 , κ_4 and the moduli K_3 and K_4 are tangent quantities.

1. The coefficient κ_1

The coefficient κ_1 is identical to the isothermal secant compressibility $\bar{\kappa}$, defined by Eq. (4).

2. The coefficient κ_2

The coefficient κ_2 is also a secant κ , which is defined as,

$$\kappa_2 \equiv (V_0^T - V_p^T) / (V_p^T p) \quad (20)$$

3. The coefficient κ_3

The coefficient κ_3 is a tangent κ , which is defined as,

$$\kappa_3 \equiv - (1 / V_0^T)(\partial V_p^T / \partial p)_T \quad (21)$$

4. The coefficient κ_4

The coefficient κ_4 is identical to the isothermal tangent compressibility as used in this paper. So,

$$\kappa_4 = \kappa = \text{tangent } \kappa_p^T \equiv - (1 / V_p^T)(\partial V_p^T / \partial p)_T \\ = (1 / \rho_p^T)(\partial \rho_p^T / \partial p)_T \quad (22)$$

From the above given definitions for κ_1 through κ_4 it follows that all κ 's are identical at atmospheric pressure (applied pressure $p = 0$)

$$\kappa_1 = \kappa_2 = \kappa_3 = \kappa_4 \quad (23)$$

We believe that κ_2 , κ_3 , K_2 , and K_3 are – like α_2 and α_3 – confusing and completely redundant. Again we strongly prefer the use of κ_1 and K_1 as the isothermal secant compressibility $\bar{\kappa}$ and the isothermal secant bulk modulus \bar{K} , and the κ_4 and K_4 as the isothermal tangent compressibility κ and the isothermal tangent bulk modulus K . The quantities κ_1 , K_1 , and α_1 are *mean* values as they are measured; κ_4 , K_4 , and α_4 are *true* values as they are calculated. There is no scientific necessity for other quantities.

The values for the isothermal secant bulk modulus K of mercury are from the work of Hayward⁸ and of Davis and Gordon.⁹ Hayward used a direct static method; he determined the isothermal secant bulk modulus of mercury for one single point at 293.145 K and at an applied pressure of 19.2 MPa with a claimed uniquely high accuracy of within 0.4%, so we use it as a reference against the isothermal secant bulk modulus of Davis and Gordon,⁹ calculated by us at precisely the same temperature and pressure from Davis and Gordon's density values. They used an indirect, dynamic method; their density determinations of mercury were based on precision ultrasonic-velocity measurements and thermodynamic data, with an uncertainty of 0.8%, for three temperatures and pressures up to 1.3 GPa, starting with the sound-velocity values at atmospheric pressure, taken from the work of Hubbard and Loomis.⁶ We consider the single value for \bar{K} , taken from Hayward, as the most accurate known value for the isothermal secant bulk modulus. Therefore, in order to determine the most accurate value for \bar{K} , we *combine* Hayward's \bar{K} with Davis and Gordon's \bar{K} , calculating the weighed mean in relation to the claimed accuracies.

The calculation of the \bar{K} of Davis and Gordon⁹ at the above-mentioned temperature and pressure has been carried out as follows. From the values of the density ρ_p^T at 295.037, 313.630, and 326.026 K, we calculate the isothermal secant bulk modulus \bar{K} from 100 through 300 MPa. For the calculation of \bar{K} at atmospheric pressure, we express the density ρ_p^T for the three above-mentioned temperatures:

$$\rho_p^T = a + b p + c p^2 + d p^3, \quad (24)$$

where the coefficients are temperature dependent. At zero pressure we obtain

$$\bar{K} = a / b. \quad (25)$$

For each of the four pressures (0, 100, 200, and 300 MPa) the value of \bar{K} for 293.145 K is computed by a *temperature* extrapolation based on a second degree polynomial in T . Through the four \bar{K} values at 293.145 K a third degree *pressure* polynomial,

$$\bar{K} = 24952.2 + 4.7980 p - 9.53 \times 10^{-5} p^2 - 4.93 \times 10^{-8} p^3, \quad (26)$$

is obtained, where \bar{K} and the applied pressure p are in MPa. This equation is represented by the dashed curve in Fig. 1. At an applied pressure of 19.2 MPa Eq. (26) yields a value for \bar{K} of 25044 MPa, which is shown by an open triangle in Fig. 1. At an applied pressure of 19.2 MPa and the same temperature, Hayward found 25170 MPa, shown by a filled square in Fig. 1. The difference between the value of Hayward⁸ and Davis and Gordon⁹ is 0.5%. The accuracy of Hayward's result is estimated to be twice that of Davis and Gordon.⁹ If we apply this estimate, we find the weighed mean point of \bar{K} at 293.145 K and 19.2 MPa applied pressure as $(2 \times 25170 + 1 \times 25044) / 3 = 25128$ MPa. The corresponding point in Fig. 1 is indicated by an open circle. Subsequently we assume that the final curve, for \bar{K} versus p , shown by a solid curve is obtained by a parallel shift over 84 MPa of the dashed curve of Davis and Gordon⁹ towards the weighed mean point. Furthermore, we assume that for all temperatures in the range 293–323 K and all the applied pressures in the range 0–400 MPa, the values for \bar{K} of Davis and Gordon⁹ must be increased by 84 MPa. The corrected values for the isothermal secant bulk modulus \bar{K} at the measured temperatures of Davis and Gordon⁹ are given in Table 4. To avoid errors on the boundary of 300 MPa, we include the experimental point of 400 MPa, also taken from the work of Davis and Gordon⁹ only for the calculation of our Equation of State.

2.5. Density of Mercury

The corrected values for the density of mercury are calculated from Eq. (27).

$$\rho_p^T = \rho_0^T / (1 - p / \bar{K}), \quad (27)$$

where \bar{K} is the *corrected* isothermal secant bulk modulus. The results are given in Table 5.

Comparing the original values of the density as stated by Davis and Gordon⁹ with the values in Table 5, we see that the corrected values in the range 0–300 MPa are up to 0.53 kg/m³ or relatively 40×10^{-6} , lower, except of course at 0 MPa.

Finally, through the fifteen values of the density ρ_p^T given in Table 5 and additionally nine values of the density at atmospheric pressure in the temperature range 293–333 K according to Ambrose,¹⁸ we calculated a double polynomial fit with eight coefficients, Eq. (28). The values of the density coefficients C_{ij} are given in Table 6, where T is in K and the applied

pressure p in MPa. The calculated RMS deviation of ρ_p^T in Eq. (28) is 0.000 kg/m³ or relatively 0.6×10^{-6} . By computation of the $(\partial \rho / \partial p)_T$ we also calculated the RMS deviation of the applied pressure p : 0.015 MPa.

$$\rho_p^T = \sum_{i,j} C_{ij} T^i p^j \quad (28)$$

The recommended values for the density of mercury, calculated with Eq. (28), for temperatures between 293 and 323 K and applied pressures between zero and 300 MPa are given in Table 7.

2.6. Estimated Relative Accuracy of the Density

The uncertainty of the temperature is estimated at 0.01 K and the relative error in the isothermal secant compressibility $\bar{\kappa}$ is taken^{8,30} as 0.5% in the range 0–100 MPa, increasing to 0.65% at 400 MPa. With these uncertainties as well as with the errors for $\bar{\alpha}$ and $\rho_0^{293.150}$ given in Sec. 2.3. of this paper we calculated, applying Eq. (2), the estimated relative accuracy in the density $\rho_p^{293.150}$. The result is given in Table 8. The standard deviation of the density ρ_p^T is, assuming that there is no correlation, the square root of the sum of square standard deviations of the quantities (each multiplied by a square factor) forming the density ρ_p^T . The sum of the percentages of these square values gives 100% with respect to the total square standard deviation in the density ρ_p^T . However, when stating *linear* percentages the phenomenon arises that this sum becomes more than 100% (at 100 MPa: 117%). Nevertheless, we prefer to give in Table 8 *linear* percentages. Only squaring the *linear* percentages mentioned in this Table gives the above mentioned square situation. From Table 8 we conclude that inaccurate isothermal compressibilities are by far the largest problem in reaching accurate densities of mercury at higher pressures.

For practical purposes, the relative accuracy in the density $\rho_p^{293.15}$ is, in the pressure range 0–400 MPa, in good approximation represented by

$$d\rho_p^{293.15} / \rho_p^{293.15} = 0.377 p e \quad (29)$$

where:

$$d\rho_p^{293.15} / \rho_p^{293.15} \text{ is in } 1 \times 10^{-6},$$

p in MPa and e is the percentage error in $\bar{\kappa}$.

3. Thermodynamic Properties and Recommended Values for Mercury

3.1. Calculation of the Isobaric Volume Thermal Expansion Coefficients

In this section we calculate the isobaric secant and tangent volume thermal expansion coefficient and determine the relationship between both in a special case. Applying Eqs. (3), (17), and (28) we compute the isobaric secant volume thermal expansion coefficient $\bar{\alpha}$ and the isobaric tangent volume thermal expansion coefficient α as

$$\bar{\alpha}(T,p) = -(C_{10} + C_{20}(T + T_0) + C_{11}p + C_{12}p^2) / \rho_p^T \quad (30)$$

and

$$\alpha(T,p) = -(C_{10} + 2C_{20}T + C_{11}p + C_{12}p^2) / \rho_p^T \quad (31)$$

From Eqs. (30) and (31) it follows that in case ρ_p^T depends linearly on the temperature [in Eq. (28) coefficient $C_{ij} = 0$ for $i \geq 2$], then at all temperatures

$$\bar{\alpha}(T,p) = \alpha(T,p) = -(C_{10} + C_{11}p + C_{12}p^2) / \rho_p^T \quad (32)$$

In Tables 9 and 10 we give recommended values for the isobaric secant and tangent volume thermal expansion coefficient, $\bar{\alpha}$ and α respectively, calculated with Eqs. (30) and (31).

3.2. Calculation of the Isothermal Compressibilities

In this section we calculate the isothermal secant and tangent compressibility and determine the relationship between both in some special cases. Applying Eqs. (4), (22), and (28), we compute the isothermal secant compressibility $\bar{\kappa}$ and the isothermal tangent compressibility κ as

$$\bar{\kappa}(T,p) = (C_{01} + C_{11}T + C_{02}p + C_{12}Tp + C_{03}p^2) / \rho_p^T \quad (33)$$

and

$$\kappa(T,p) = (C_{01} + C_{11}T + 2C_{02}p + 2C_{12}Tp + 3C_{03}p^2) / \rho_p^T \quad (34)$$

So, at atmospheric pressure, $p = 0$ MPa,

$$\bar{\kappa}(T,0) = \kappa(T,0) = (C_{01} + C_{11}T) / \rho_0^T \quad (35)$$

It follows from Eqs. (33) and (34) that in case ρ_p^T depends linearly on the applied pressure [in Eq. (28) coefficients $C_{ij} = 0$ for $j \geq 2$], then at all pressures

$$\bar{\kappa}(T,p) = \kappa(T,p) = (C_{01} + C_{11}T) / \rho_p^T \quad (36)$$

The identities in Eqs. (35) and (36) for the isothermal secant and tangent compressibility are also valid for the isothermal secant and tangent bulk modulus; of course with *reciprocal terms and results* on the right of the equations. In Tables 11 and 12 we give recommended values for the isothermal secant compressibility $\bar{\kappa}$ and the isothermal tangent compressibility κ , calculated with Eqs. (33) and (34). Since the accuracy of the isothermal compressibilities nowadays is at most 0.5%, there is no significant difference in values of the isothermal secant compressibility in the temperature range 293-323 K and the pressure range 0-300 MPa with respect to the temperature scales ITS-27, IPTS-48, IPTS-68, and ITS-90. This statement is also valid for the isothermal tangent compressibility.

3.3. Calculation of Thermodynamic Properties

From the Equation of State, Eq. (28); from values for the ρ_0^T given by Ambrose¹⁸ and from values for the isobaric specific heat capacity $C_{p,0}^T$ as a function of temperature T at atmo-

spheric pressure, given by Douglas *et al.*³¹ thermodynamic parameters can be computed from thermodynamic identities. We calculate recommended values for the entropy S , the enthalpy H , the isobaric specific heat capacity C_p , the internal energy U , and the isochoric specific heat capacity C_v , as a function of temperature and applied pressure. For this purpose we calculated a third degree least squares polynomial in T (Eq. 37), using the $C_{p,0}^T$ values of Douglas *et al.*³¹ at atmospheric pressure (applied pressure $p = 0$) in the range of 253-473 K.

$$C_{p,0}^T = A_0 + A_1 T + A_2 T^2 + A_3 T^3 \quad (37)$$

where:

$C_{p,0}^T$ is in $\text{J}\cdot\text{K}^{-1}\text{kg}^{-1}$, and temperature T is in K. $A_0 = 152.2958$; $A_1 = -0.0610935$; $A_2 = 5.66063 \times 10^{-5}$; $A_3 = -2.704 \times 10^{-9}$. The estimated uncertainty of $C_{p,0}^T$ is $0.4 \text{ J}\cdot\text{K}^{-1}\text{kg}^{-1}$ or 0.3%.³¹ The standard deviation of our fit is $4 \times 10^{-4} \text{ J}\cdot\text{K}^{-1}\text{kg}^{-1}$.

$$S_p^T - S_0^{298.15} = \int_{298.15}^T T^{-1} C_{p,0}^T dT + \int_0^p (\partial S / \partial p)_T dp \quad (38)$$

$$\text{where:} \quad (\partial S / \partial p)_T = -\alpha / \rho \quad (39)$$

and $S_0^{298.15}$ is put equal to zero.

$$H_p^T - H_0^{298.15} = \int_{298.15}^T C_{p,0}^T dT + \int_0^p (\partial H / \partial p)_T dp \quad (40)$$

where:

$$(\partial H / \partial p)_T = (1 - T\alpha) / \rho \quad (41)$$

and $H_0^{298.15}$ is put equal to zero.

$$C_{p,p}^T = C_{p,0}^T + \int_0^p (\partial C_p / \partial p)_T dp \quad (42)$$

where:

$$(\partial C_p / \partial p)_T = -(T/\rho) [2(\partial \rho / \partial T)_p^2 / \rho^2 - (\partial^2 \rho / \partial T^2)_p / \rho] \quad (43)$$

The integrations with respect to the temperature T at $p = 0$ MPa can be performed analytically from Eq. (37); the integrations with respect to p were performed numerically with Simpson's method. The internal energy U is calculated from

$$U_p^T = H_p^T - (p + p_0) / \rho_p^T \quad (44)$$

where: $(p + p_0)$ is the absolute pressure, p_0 being 101325 Pa. The isochoric specific heat capacity C_v is calculated from

$$C_{v,p}^T = C_{p,p}^T - T(\partial \rho / \partial T)_p^2 / \rho^2 (\partial \rho / \partial p)_T \quad (45)$$

The results for the entropy, enthalpy, C_p , internal energy, and C_v are given in the Tables 13, 14, 15, 16, and 17, respectively. To get some insight in the precision of the calculated thermodynamic quantities, we constructed a perturbation at

random on the recommended ρ_p^T values, which have a relative RMS deviation of 0.6×10^{-6} . We obtained for $\bar{\kappa}$, κ , C_p and C_v a relative RMS deviation of 273×10^{-6} , 233×10^{-6} , 46×10^{-6} , and 122×10^{-6} , respectively. Note that the relative RMS deviations for $\bar{\kappa}$ and κ are roughly the same.

3.4. Recommended Values

Recommended values are given in Tables 7 and 9–17. All temperatures are in K ITS-90.

3.5. Remark

All *relative differences* between values of authors and our recommended values are in this paper calculated in the same way. For the isothermal tangent compressibility κ : ($\kappa_{\text{author}} - \kappa_{\text{recommended value}}$) / $\kappa_{\text{recommended value}}$.

4. Comparison of the Recommended Values for Mercury With Data in Literature

4.1. Isothermal Tangent and Secant Compressibility at Atmospheric Pressure

From velocity of sound measurements at atmospheric pressure, by several authors the isothermal tangent compressibility κ was determined by us. In all cases we *recalculated* the values for κ from the experimental velocity of sound data and the thermodynamic data mentioned below. In order to make a relevant comparison possible, we always used thermodynamic data from the same sources. The κ at atmospheric pressure is computed according to

$$\kappa = 1 / (\rho_0^T v^2) + \alpha^2 T / (\rho_0^T C_{p,0}^T) \quad (46)$$

where:

- κ is the isothermal *tangent* compressibility in Pa^{-1} ,
- ρ_0^T is the density at atmospheric pressure in kg/m^3 ,
- v is the velocity of sound in m/s ,
- α is the isobaric *tangent* volume thermal expansion coefficient at atmospheric pressure in K^{-1} ,
- T is the absolute temperature in K,
- $C_{p,0}^T$ is the isobaric specific heat capacity at atmospheric pressure in $\text{J}\cdot\text{K}^{-1} \text{kg}^{-1}$.

The results for the isothermal tangent compressibility are represented by a least squares polynomial in the temperature T , where in some cases, in view of the value of the standard deviation of the linear fit, it was necessary to use a quadratic fit. In the following equations the isothermal compressibility is expressed in MPa^{-1} and the temperature T in K. Before paying attention to the dynamic isothermal tangent κ equations at atmospheric pressure we mention a few secant $\bar{\kappa}$ equations at atmospheric pressure based on the static method of isothermal compressibility determination. We stress that at atmospheric pressure (applied pressure $p = 0$) the tangent κ and the secant $\bar{\kappa}$ are equal; we refer to Eqs. (23) and (35). Behind the author's name the temperature range used is mentioned.

4.1.1. Static Measurements

Bridgman (1911)(a)^{7a}; temperature range 273–295 K:
 $\kappa = 2.0178 \times 10^{-5} + 67.557 \times 10^{-9} T$ (47)

Diaz Peña and McGlashan³²; temperature range 283–328 K:
 $\kappa = 2.840 \times 10^{-5} + 40.22 \times 10^{-9} T$ (48)

Stallard, Rosenbaum, and Davis¹¹; temperature range 293–363 K:
 $\kappa = 2.6325 \times 10^{-5} + 47.391 \times 10^{-9} T$ (49)

Grindley and Lind, Jr.¹²; temperature range 303–423 K:
 $\kappa = 8.106 \times 10^{-6} + 148.749 \times 10^{-9} T - 13.6176 \times 10^{-11} T^2$ (50)

4.1.2. Dynamic Measurements

Hubbard and Loomis⁶; temperature range 273–343 K:
 $\kappa = 2.8714 \times 10^{-5} + 30.922 \times 10^{-9} T + 27.75 \times 10^{-12} T^2$ (51)

Kleppa³³; temperature range 323–423 K:
 $\kappa = 2.05 \times 10^{-5} + 64.8 \times 10^{-9} T$ (52)

Golik, Kassen and Kuchak³⁴; temperature range 293–373 K:
 $\kappa = 3.0290 \times 10^{-5} + 24.865 \times 10^{-9} T + 29.48 \times 10^{-12} T^2$ (53)

Hunter, Welch, and Montrose³⁵; temperature range 298–403 K:
 $\kappa = 2.7484 \times 10^{-5} + 32.125 \times 10^{-9} T + 36.31 \times 10^{-12} T^2$ (54)

Seemann and Klein³⁶; temperature range 253–333 K:
 $\kappa = 2.8224 \times 10^{-5} + 34.240 \times 10^{-9} T + 21.79 \times 10^{-12} T^2$ (55)

Hill and Ruoff³⁷; temperature range 303–470 K:
 $\kappa = 2.4552 \times 10^{-5} + 52.898 \times 10^{-9} T$ (56)

Coppens, Beyer, and Ballou³⁸; temperature range 303–472 K:
 $\kappa = 3.0077 \times 10^{-5} + 23.599 \times 10^{-9} T + 37.090 \times 10^{-12} T^2$ (57)

Tilford³⁹; temperature range 294–302 K:
 $\kappa = 2.8518 \times 10^{-5} + 33.407 \times 10^{-9} T + 21.68 \times 10^{-12} T^2$ (58)

Using our Equation of State (Eq. 28) we first computed the isothermal tangent and secant compressibility (which are numerically the same at atmospheric pressure) as a function of temperature at atmospheric pressure. Then we calculated a second degree polynomial in T through the compressibility points, so deriving a *recommended equation* (Eq. 59) for the isothermal tangent and secant compressibility at atmospheric pressure in the temperature range 293–323 K:

$$\kappa = 2.7018 \times 10^{-5} + 41.909 \times 10^{-9} T + 7.52 \times 10^{-12} T^2 \quad (59)$$

For a comparison at atmospheric pressure of the values of the isothermal tangent and secant compressibility of Hubbard

^aWe refer to Sec. 4.3.2.

and Loomis,⁶ Coppens *et al.*,³⁸ Grindley and Lind, Jr.,¹² and our recommended values from Eq. (59) we refer to Fig. 2; for an analogue comparison between Bridgman (1911),⁷ Seemann and Klein,³⁶ Diaz Peña and McGlashan,³² and our recommended values from Eq. (59) we refer to Fig. 3.

4.2. Error in Isothermal Tangent and Secant Compressibility and in $(\partial\kappa/\partial T)_p$ and $(\partial\bar{\kappa}/\partial T)_p$ at Atmospheric Pressure

First we briefly discuss errors occurring in the dynamic method. Several authors claim a precision / uncertainty for the velocity of sound in mercury of about 200×10^{-6} , except Tilford³⁹ who gives an uncertainty of 10×10^{-6} . The uncertainty of κ in Eq. (46) [when estimating the uncertainty in the velocity of sound at the usual claimed value of 200×10^{-6}] is for over 50% caused by the uncertainty in the following thermodynamic data: the isobaric specific heat capacity $C_{p,0}^T$, the isobaric tangent volume thermal expansion coefficient α , the density ρ_0^T , and the absolute temperature T . The uncertainty in these thermodynamic data is for over 90% caused by the uncertainty in the $C_{p,0}^T$. Calculating the precision at atmospheric pressure of the isothermal tangent compressibility κ in Eq. (46) we found about 0.002×10^{-5} MPa⁻¹ or about 0.05%. However, according to Hayward,³⁰ an accuracy of 1% is the most that can be reached for values of the isothermal compressibility, derived from velocity of sound measurements. In Table 18 we give the difference in isothermal tangent and secant compressibility at atmospheric pressure between the values of the authors mentioned above and our recommended values at 293.15 and 323.15 K. Also the applied method is given. The difference between the mean values of the isothermal compressibilities at 293.15 and 323.15 K of the authors and our recommended values is 0.4 and 0.6%, respectively. Our estimated accuracy for the isothermal tangent and secant compressibility at atmospheric pressure in the temperature range 293.15–323.15 K is 0.5%. In Table 19 we provide, by stating values obtained by both methods, a comparison at atmospheric pressure of the derivatives $(\partial\kappa/\partial T)_p$ and $(\partial\bar{\kappa}/\partial T)_p$ at — where measured — 293.15, 303.15, 323.15, and 423.15 K between several authors and our recommended values. Also the relative standard deviations (1σ) with respect to the mean values are mentioned. Using the thermodynamic identity

$$(\partial\kappa/\partial T)_p = -(\partial\alpha/\partial p)_T \quad (60)$$

we calculate the isobaric tangent volume thermal expansion coefficient α at higher pressures. Eq. (60) may be used for the density determination at higher pressures according to the dynamic method (Davis and Gordon⁹).

4.3. Comparisons at Higher Pressures

4.3.1. Introduction

Bett, Hayes, and Newitt⁴⁰ published in their paper a critical review and comparison of results of isothermal compressibility determinations of mercury at 293.15 K from the end of the

19th century till 1950. Hayward³⁰ compared and briefly discussed the results of ten isothermal secant compressibility measurements of mercury; eight have been carried out according to the static method and two according to the dynamic method. Hayward's values at 293.15 K scatter over a band just under 10% wide.

For our comparisons at 293.15 K we confine ourselves to the results of six papers: Bridgman (1911)⁷ (a), Bett, Weale, and Newitt,¹⁰ Stallard, Rosenbaum, and Davis, Jr.,¹¹ Grindley and Lind Jr.,¹² Vukalovich *et al.*,¹³ and Kumari and Dass.¹⁴

4.3.2. Bridgman (1911)^a

Bridgman (1911)⁷, who used a static method, discusses only volumes and volume differences; hence all isothermal secant and tangent compressibilities and densities of mercury were calculated by us. Values in his paper are mentioned in several places; these values, however, may show differences varying from zero up to 0.6% and even more. We adopted the values which Bridgman states to be 'more accurate'; we call them the (a) values. The isothermal secant compressibility $\bar{\kappa}$ is calculated in the usual way; the isothermal tangent compressibility κ is deduced from the secant one by the following equation

$$\kappa = (\bar{\kappa} + p(d\bar{\kappa}/dp)) / (1 - \bar{\kappa}p) \quad (61)$$

where p is the applied pressure; this equation may be derived from Eq. (2). For a comparison of $\bar{\kappa}$, κ and ρ_p^T between the results of Bridgman (1911)(a) and our recommended values we refer to Figs. 4 through 7. It is of interest to compare the precision of the isothermal secant $\bar{\kappa}$ and the isothermal tangent κ at the same applied pressure p and temperature T . We investigated this problem by constructing a perturbation on $\bar{\kappa}$ in Eq. (61), varying from 1 to 10% in the ranges 293 to 323 K and 0 to 300 MPa. It was found that the precisions of $\bar{\kappa}$ and κ were practically the same. This result is in agreement with the remark at the end of Sec. 3.3.

4.3.3. Bett, Weale, and Newitt

Bett, Weale, and Newitt¹⁰ published revised values for the isothermal secant compressibility of liquid mercury from 243 to 423 K and up to 1176 MPa. These values have been obtained by using the equation of Hudleston to correlate the static secant measurements of Bridgman (1911)⁷ with the dynamic tangent determinations at atmospheric pressure of Hubbard and Loomis,⁶ supplemented with one value of Kleppa.³³ In Figs. 8 and 9 we show the isothermal secant and tangent compressibility, respectively, as a function of the applied pressure. In Fig. 10 we give the percentage difference of the isothermal secant and tangent compressibility between the values of Bett, Weale, and Newitt and our recommended values. In Fig. 10 we also give the relative standard deviation

^aAn unpublished paper, containing a critical, more detailed analysis of the compressibility measurements of liquid mercury up to 700 MPa, stated in the paper of Bridgman (1911),⁷ has been written; it is available at the Van der Waals-Zeeman Laboratory.

(1σ) of the isothermal secant compressibility as a function of applied pressure as calculated by Bett, Hayes and Newitt.⁴⁰ The values of the isothermal compressibilities of Bett, Weale, and Newitt¹⁰ and our recommended values are correlated: both partly depend on Hubbard and Loomis.^{6,9} The use of empirical compressibility equations for liquids (e.g. Tait, Hudleston, MacDonald) has been critically discussed by Hayward.⁴¹

4.3.4. Stallard, Rosenbaum, and Davis, Jr.

Stallard, Rosenbaum, and Davis, Jr.¹¹ measured compressibilities from 293 to 363 K and over a pressure range of 0–200 MPa. Careful study of their paper convinced us that the mentioned isothermal compressibilities were isothermal *tangent secant* compressibilities. Their measuring device consists of two connected similar cylindrical tubes, which are filled with mercury. In the first tube the velocity of sound is determined by measuring the time of flight of an ultrasonic pulse over a path of known length; in the second tube the time of flight is measured again. Using the just calculated velocity, the variable height of the mercury column in the second tube can be computed. So in essence they used a *static* method. Though we believe that their results at higher pressures are low, we nevertheless have the opinion that they used an ingenious method. For a comparison of the results of Bett, Weale, and Newitt,¹⁰ Stallard *et al.*,¹¹ and our recommended values, we refer to Figs. 8 and 9.

4.3.5. Grindley and Lind, Jr.

Grindley and Lind, Jr.,¹² using a static method, measured *pVT* properties of mercury and report densities as a function of pressure and temperature. From these values we calculated the isothermal secant and tangent compressibilities. The isothermal tangent / secant compressibilities on the isobar at atmospheric pressure as a function of temperature of Hubbard and Loomis,⁶ Coppens *et al.*³⁸ and Grindley and Lind, Jr.¹² are compared with our recommended values in Fig. 2. For further comparison of the results of $\bar{\kappa}$, κ , and ρ_p^T – and the relative differences between both $\bar{\kappa}$'s, κ 's and ρ_p^T 's – from Bridgman⁷ and Grindley and Lind, Jr.¹² and our recommended values we, again, refer to Figs. 4 through 7. Above-mentioned values at 293.15 K of Grindley and Lind, Jr.¹² are extrapolations as carried out by us in this paper. Remarkable is the good agreement at 293.15 K in isothermal compressibilities and density between the values of Bridgman (1911)(a) and the values of Grindley and Lind, Jr.¹²

Grindley and Lind, Jr.¹², stating that the pressure is measured on a Harwood manganin gauge, which is periodically calibrated at the freezing point of mercury at 273.15 K, using the international standard of 756.9 MPa (located to ± 0.15 MPa), claim a precision of measurement of 0.02 MPa at all pressures. In their Table III Grindley and Lind, Jr.¹² present a nine-parameter double polynomial Equation of State, $p_{\text{calc}}(T, p)$. We investigated the fit of this function to *all* of the (p, T, ρ) data of their Table II; the standard deviation of the pressure $\Delta p = p - p_{\text{calc}}(T, p)$ was found to be 0.86 MPa (the

largest $|\Delta p|$ is about twice that); the relative standard deviation of the density, calculated by

$$10^6 \cdot \Delta \rho_p^T / \rho_p^T = 10^6 \cdot \Delta p / (\rho_p^T \cdot \partial p_{\text{calc}} / \partial \rho_p^T), \quad (62)$$

yielded 32×10^{-6} . For the RMS difference between the values of thermodynamic properties of mercury of Grindley and Lind, Jr.¹² (calculated by us in the same way as our thermodynamic properties, for the same temperature and pressure range) and the recommended values, we refer to Table 20. For the values of the C_v at 303.15 K as a function of the specific volume from Grindley and Lind, Jr.¹² compared with our recommended values, we refer to Fig. 11.

4.3.6. Vukalovich *et al.*

In their review monograph Vukalovich *et al.*¹³ state many values of thermophysical properties of mercury as a function of temperature and pressure. Values for the density, the isobaric tangent volume thermal expansion coefficient, the isothermal tangent compressibility, the entropy, the enthalpy, and the specific heat capacities C_p and C_v are mentioned in their Tables 16, 17, 18, 21, 20, 22, and 23, respectively. For the RMS difference between the values of thermodynamic properties of mercury of Vukalovich *et al.* (calculated by us in the same way as our thermodynamic properties, for the same temperature and pressure range) and our recommended values we refer to Table 21.

4.3.7. Kumari and Dass

Kumari and Dass¹⁴ derived a theoretical Equation of State for mercury based on the assumption that the ratio of second to first pressure derivative of the tangent bulk modulus is a constant. Though there is some correlation between the work of Kumari and Dass¹⁴ and ours – Kumari and Dass¹⁴ used the measurements of Davis and Gordon⁹ to fit their Equation of State – the excellent agreement is nevertheless remarkable. The difference between the densities (ranges 303–323 K, 0–300 MPa) is given in Fig. 12. For the RMS difference between the values of thermodynamic properties of mercury of Kumari and Dass¹⁴ (calculated by us in the same way as our thermodynamic properties, for the same temperature and pressure range) and our recommended values, we refer to Table 22.

5. Comparison of the Results of the Work on Mercury of Davis and Gordon, and Grindley and Lind, Jr.

We try to make some comparisons, first at atmospheric pressure. Hubbard and Loomis' Eq. (51) has a standard deviation for κ of 0.003%; the temperature range is 273.15–343.15 K. Eq. (57) of Coppens, Beyer, and Ballou³⁸ has a standard deviation for κ of 0.01%; the temperature range is about 303–472 K. The agreement in κ between Hubbard and Loomis,⁶ and Coppens, Beyer, and Ballou³⁸ is excellent. In the overlap temperature range 303–343 K the mean difference in

κ is only 0.06%. Eq. (50) of Grindley and Lindt, Jr.¹² has a standard deviation for $\bar{\kappa}$ of 1%; the temperature range is 303–423 K. We refer to Fig. 2. Thus the precision of the initial isothermal compressibility at atmospheric pressure of Hubbard and Loomis⁶ / Davis and Gordon⁹ seems higher than that of Grindley and Lind, Jr.¹² Now we compare the ρ_p^T of Davis and Gordon,⁹ and Grindley and Lind, Jr.¹², also at higher pressures. From Davis and Gordon⁹ we consider the pressure range 0–800 MPa and the three temperatures 295.037, 313.630, and 326.026 K; from Grindley and Lind, Jr.¹² we consider the pressure range 0–800 MPa and the temperatures 303.134, 313.130, 323.127, and 333.124 K.

For each of the series measurements we calculated a double polynomial equation ρ_p^T ; the best possible fit was the only criterion. For Davis and Gordon⁹ we found a standard deviation of ρ_p^T of 0.05 kg/m³ and a relative standard deviation of 4×10^{-6} . For Grindley and Lind, Jr.¹² we found a standard deviation of ρ_p^T of 0.40 kg/m³ and a relative standard deviation of 29×10^{-6} . By determining the $(\partial\rho/\partial p)_T$ we calculated the

standard deviation of the applied pressure p . For Davis and Gordon,⁹ and Grindley and Lind, Jr.¹² we found 0.10 MPa and 0.80 MPa, respectively. Davis and Gordon⁹ state a standard deviation for the pressure (in the range 0–1.3 GPa) of 0.6 MPa. Comparing the densities of Davis and Gordon,⁹ and Grindley and Lind, Jr.¹² in the ranges 0–800 MPa and 298.15–328.15 K we found a RMS difference of 2.70 kg/m³ and a relative RMS difference of 200×10^{-6} . Except a few values at atmospheric pressure, all *calculated* density values of Grindley and Lind, Jr.¹² are higher than those of Davis and Gordon.⁹ Assuming that no smoothing has been carried out, the *precision* of the measurements of Davis and Gordon⁹ seems higher than that of Grindley and Lindt, Jr.¹² However, the above-mentioned calculations do not inform us on the *accuracy* of both density determinations.

The value of the density of mercury at 303.15 K and 300 MPa applied pressure of Davis and Gordon⁹ is 13678.57 kg/m³; the corresponding value of Grindley and Lind, Jr.¹² is about 1.33 kg/m³ or 100×10^{-6} higher.

TABLE 1. Determinations of the density of mercury at 293.150 K and one standard atmosphere

Author	Applied method	Density of mercury, kg/m ³			Relative uncertainty ^a
		IPTS-48	IPTS-68	ITS-90	
Cook and Stone ^b	displacement / content	13545.884	13545.867	13545.854	0.2×10^{-6}
Cook ^c					
Ippitz ^d	content,	13545.839	13545.822	13545.809	2×10^{-6}
Kuzmenkov ^e	relative hybrid	13545.91	13545.89	13545.88	2×10^{-6}
Fürtig ^{f,g,h}	displacement	—	13545.849	13545.836	$1-1.5 \times 10^{-6}$
[3 samples]					
Adametz ^{g,h}	displacement	—	13545.876	13545.863	2×10^{-6}
[2 samples]					
Adametz and Wloka ^b	displacement	—	13545.849	13545.836	1×10^{-6}
[3 samples: VNIIFTRI, NIST, PTB]					

^a Assumed that uncertainty means one standard deviation.

^b Ref. 1.

^c Ref. 2.

^d Ref. 3.

^e Ref. 22.

^f Ref. 23.

^g Ref. 21

^h Ref. 24

TABLE 2. Impurities in mercury from the Van der Waals-Zeeman Laboratory

Metal	Quantity in ppb
Ag	15-150
Cu	<100
Fe	10-100
Cd	<5
Al	<500
Pb	<25
Zn	10-100

TABLE 3. Results of the four versions of the isobaric volume thermal expansion coefficient of mercury at atmospheric pressure applied to three temperatures from Davis and Gordon⁹

Temperature K	Secant α_1 $\times 10^6$, K^{-1} Eq.(8)	Secant α_2 $\times 10^6$, K^{-1} Eqs.(13) and (8)	Tangent α_3 $\times 10^6$, K^{-1} Eqs.(16) and (8)	Tangent α_4 $\times 10^6$, K^{-1} Eqs.(18) and (8)
295.037	181.723	181.003	181.877	181.156
313.630	181.866	180.537	182.205	180.873
326.026	181.976	180.241	182.467	180.728

TABLE 4. Corrected isothermal secant bulk moduli \bar{K} from Davis and Gordon,⁹ MPa

Temperature K	Applied pressure in MPa				
	0	100	200	300	400
295.037	24977	25457	25935	26411	26896
313.630	24432	24915	25399	25884	26367
326.026	24101	24582	25062	25539	26024

TABLE 5. Corrected densities of mercury, reference values for Eq. (28)

Temperature K	Applied pressure, MPa				
	0	100	200	300	400
	Corrected density of mercury, kg/m^3				
295.037	13541.22	13594.62	13646.46	13696.80	13745.65
313.630	13495.73	13550.12	13602.84	13653.98	13703.63
326.026	13465.51	13520.51	13573.83	13625.57	13675.71

TABLE 6. Density coefficients C_{ij} of Eq. (28)

$i \setminus j$	0	1	2	3
0	14288.8433	0.3859641	-3.38435×10^{-5}	9.237×10^{-9}
1	-2.6164300	5.294163×10^{-4}	-1.61081×10^{-7}	
2	2.793555×10^{-4}			

TABLE 7. Density of mercury, kg/m^3

Applied pressure MPa	Temperature K						
	293.150	298.150	303.150	308.150	313.150	318.150	323.150
0	13545.84	13533.59	13521.35	13509.12	13496.90	13484.70	13472.52
50	13572.70	13560.57	13548.46	13536.36	13524.28	13512.21	13500.15
100	13599.16	13587.16	13575.17	13563.20	13551.24	13539.30	13527.37
150	13625.23	13613.35	13601.48	13589.64	13577.80	13565.98	13554.17
200	13650.91	13639.15	13627.40	13615.67	13603.96	13592.25	13580.56
250	13676.21	13664.57	13652.94	13641.32	13629.72	13618.13	13606.55
300	13701.15	13689.61	13678.09	13666.58	13655.09	13643.61	13632.15

TABLE 8. Estimated relative accuracy of the density $\rho_p^{293.15}$ of mercury. Percentage error in the density $\rho_p^{293.15}$ due to the error in $\bar{\kappa}$

Applied Pressure MPa	Estimated relative accuracy $\rho_p^{293.15}$	linear percentage of error in $\bar{\kappa}$ term / error in $\rho_p^{293.15}$ %
0	2×10^{-6}	0.00
10	3×10^{-6}	64.89
50	10×10^{-6}	97.33
100	20×10^{-6}	99.30
200	43×10^{-6}	99.85
300	69×10^{-6}	99.94
400	98×10^{-6}	99.97

TABLE 9. Isobaric *secant* volume thermal expansion coefficient $\bar{\alpha}(T,p) \times 10^6, \text{K}^{-1}$

Applied pressure MPa	Temperature K						
	293.150	298.150	303.150	308.150	313.150	318.150	323.150
0	181.475	181.536	181.597	181.658	181.719	181.780	181.841
50	179.195	179.252	179.310	179.367	179.424	179.481	179.537
100	176.989	177.042	177.096	177.149	177.202	177.256	177.309
150	174.855	174.905	174.955	175.005	175.055	175.104	175.154
200	172.794	172.840	172.887	172.933	172.979	173.026	173.072
250	170.803	170.847	170.890	170.933	170.976	171.019	171.062
300	168.884	168.924	168.964	169.004	169.044	169.084	169.124

TABLE 10. Isobaric *tangent* volume thermal expansion coefficient $\alpha(T,p) \times 10^6, K^{-1}$

Applied pressure MPa	Temperature K						
	293.150	298.150	303.150	308.150	313.150	318.150	323.150
0	181.062	181.020	180.977	180.934	180.891	180.848	180.804
50	178.784	178.737	178.691	178.644	178.597	178.550	178.503
100	176.578	176.528	176.478	176.428	176.378	176.327	176.276
150	174.445	174.392	174.339	174.285	174.232	174.178	174.123
200	172.384	172.328	172.272	172.215	172.158	172.101	172.043
250	170.395	170.336	170.276	170.216	170.156	170.096	170.035
300	168.476	168.414	168.352	168.289	168.226	168.163	168.099

TABLE 11. Isothermal *secant* compressibility $\bar{\kappa}(T,p) \times 10^5, MPa^{-1}$

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	3.995	4.018	4.041	4.065	4.088	4.111	4.135
50	3.957	3.980	4.003	4.026	4.049	4.072	4.095
100	3.920	3.943	3.965	3.988	4.010	4.033	4.055
150	3.884	3.906	3.928	3.950	3.972	3.994	4.016
200	3.848	3.870	3.891	3.913	3.935	3.956	3.978
250	3.813	3.834	3.855	3.877	3.898	3.919	3.940
300	3.778	3.799	3.820	3.841	3.862	3.882	3.903

TABLE 12. Isothermal *tangent* compressibility $\kappa(T,p) \times 10^5, MPa^{-1}$

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	3.995	4.018	4.041	4.065	4.088	4.111	4.135
50	3.928	3.950	3.973	3.995	4.018	4.040	4.063
100	3.862	3.884	3.906	3.927	3.949	3.971	3.993
150	3.798	3.819	3.840	3.861	3.882	3.903	3.924
200	3.735	3.755	3.775	3.796	3.816	3.837	3.857
250	3.673	3.693	3.712	3.732	3.752	3.771	3.791
300	3.613	3.632	3.651	3.670	3.689	3.708	3.726

TABLE 13. Entropy, $S_p^T - S_0^{298.15}, J \cdot K^{-1} \text{ mol}^{-1}$

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	-0.47193	0.00000	0.46361	0.91919	1.36699	1.80729	2.24031
50	-0.60501	-0.13317	0.33036	0.78585	1.23357	1.67377	2.10671
100	-0.73617	-0.26441	0.19903	0.65444	1.10208	1.54220	1.97506
150	-0.86549	-0.39380	0.06957	0.52490	0.97246	1.41252	1.84530
200	-0.99301	-0.52140	-0.05810	0.39716	0.84466	1.28464	1.71735
250	-1.11881	-0.64726	-0.18403	0.27117	0.71860	1.15851	1.59116
300	-1.24295	-0.77146	-0.30829	0.14685	0.59422	1.03407	1.46666

TABLE 14. Enthalpy, $H_p^T - H_0^{298.15}$ kJ·mol⁻¹

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	-0.13952	0.00000	0.13938	0.27862	0.41773	0.55671	0.69555
50	0.56114	0.70064	0.83999	0.97921	1.11829	1.25724	1.39606
100	1.26092	1.40039	1.53972	1.67891	1.81797	1.95689	2.09568
150	1.95981	2.09926	2.23857	2.37774	2.51677	2.65567	2.79444
200	2.65783	2.79726	2.93655	3.07569	3.21470	3.35358	3.49233
250	3.35498	3.49439	3.63366	3.77279	3.91178	4.05063	4.18936
300	4.05127	4.19067	4.32992	4.46903	4.60800	4.74684	4.88554

TABLE 15. Isobaric specific heat capacity $C_{p,p}^T$, J·K⁻¹ mol⁻¹

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	27.919	27.890	27.862	27.835	27.808	27.782	27.756
50	27.914	27.885	27.857	27.830	27.803	27.777	27.751
100	27.909	27.880	27.852	27.825	27.798	27.771	27.746
150	27.904	27.876	27.848	27.820	27.793	27.767	27.741
200	27.900	27.872	27.843	27.816	27.789	27.762	27.736
250	27.896	27.868	27.839	27.812	27.785	27.758	27.732
300	27.893	27.864	27.836	27.808	27.781	27.754	27.728

TABLE 16. Internal energy U_p^T , J·mol⁻¹

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	-141.02	-1.50	137.88	277.12	416.23	555.20	694.04
50	-179.30	-40.47	98.23	236.78	375.20	513.48	651.63
100	-215.60	-77.43	60.60	198.49	336.24	473.85	611.34
150	-249.98	-112.45	24.93	162.16	299.27	436.23	573.07
200	-282.51	-145.62	-8.87	127.74	264.21	400.55	536.76
250	-313.27	-176.99	-40.85	95.15	231.01	366.73	502.33
300	-342.32	-206.63	-71.09	64.32	199.58	334.71	469.71

TABLE 17. Isochoric specific heat capacity $C_{v,p}^T$, J·K⁻¹ mol⁻¹

Applied pressure MPa	Temperature K						
	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0	24.356	24.287	24.218	24.150	24.083	24.017	23.952
50	24.388	24.318	24.250	24.182	24.116	24.050	23.985
100	24.418	24.349	24.280	24.213	24.146	24.081	24.017
150	24.446	24.377	24.309	24.242	24.175	24.110	24.046
200	24.473	24.404	24.336	24.269	24.203	24.138	24.073
250	24.498	24.429	24.361	24.294	24.228	24.163	24.099
300	24.521	24.452	24.384	24.318	24.252	24.187	24.123

TABLE 18. Relative difference in isothermal tangent and secant compressibility at 293.15 K and 323.15 K, and at atmospheric pressure between data from literature and our recommended values

Author	Relative difference in isothermal compressibility %	
	293.15 K	323.15 K
Static method		
Bridgman (1911)(a) ^{ab}	+ 0.1	—
Diaz Peña and McGlashan ^b	+ 0.6	+ 0.1
Stallard, Rosenbaum, and Davis, Jr. ^b	+ 0.7	+ 0.7
Grindley and Lind, Jr. ^b	+ 0.1 ^c	+ 1.5
Dynamic method		
Hubbard and Loomis ^b	+ 0.5	+ 0.6
Kleppa ^b	—	+ 0.3
Golik, Kassen, and Kuchak ^b	+ 0.4	+ 0.1
Hunter, Welch, and Montrose ^b	+ 0.2 ^c	+ 0.8
Seemann and Klein ^b	+ 0.5	+ 0.5
Hill and Ruoff ^b	+ 0.3 ^c	+ 0.7
Coppens, Beyer, and Ballou ^b	+ 0.6 ^c	+ 0.6
Tilford ^b	+ 0.6 ^c	—
Recommended Values $\kappa \times 10^5$, MPa ⁻¹ Eq. (59)	3.995	4.135

^aWe refer to Sec. 4.3.2.^bFor references: Eqs. (47) - (58)^cAs extrapolated in this paperTABLE 19. Comparison of the derivatives $(\partial\kappa/\partial T)_p$ and $(\partial R/\partial T)_p$ ^d at several temperatures and at atmospheric pressure between data from literature and our recommended values

	$(\partial\kappa/\partial T)_p \times 10^9$, MPa ⁻¹ K ⁻¹			
	Temperature			
	293.15 K	303.15 K	323.15 K	423.15 K
Static method				
Bridgman (1911)(a) ^{ab}	68	68 ^c	—	—
Diaz Peña and McGlashan ^b	40	40	40	—
Stallard, Rosenbaum, and Davis ^b	47	47	47	—
Grindley and Lind, Jr. ^b	69 ^c	66	61	34
Dynamic method				
Hubbard and Loomis ^b	47	48	49	—
Kleppa ^b	—	—	65	65
Golik, Kassen, and Kuchak ^b	42	43	44	—
Hunter, Welch, and Montrose ^b	53 ^c	54	56	63 ^c
Seemann and Klein ^b	47	47	48	—
Hill and Ruoff ^b	53 ^c	53	53	53
Coppens, Beyer, and Ballou ^b	45 ^c	46 ^c	48	55
Tilford ^b	46 ^c	47 ^c	—	—
Recommended values, Eq. (59)	46	46	47	—
Mean all values	50	50	51	54
Relative standard deviation	18 %	17 %	15 %	23 %

^aWe refer to Sec. 4.3.2.^bFor references: Eqs. (47) - (58)^cAs extrapolated in this paper^dAt atmospheric pressure $(\partial\kappa/\partial T)_p$ and $(\partial R/\partial T)_p$ are identical

A CRITICAL EVALUATION OF THE THERMOPHYSICAL PROPERTIES OF MERCURY

TABLE 20. RMS difference between values on mercury of Grindley and Lind, Jr. and our recommended values. Ranges 293–323 K and 0–300 MPa

Thermodynamic properties	RMS difference	Relative RMS difference
Density, kg/m ³	1.2	85×10 ⁻⁶
Secant thermal expansion coefficient × 10 ⁶ , K ⁻¹	2.1	1.2 %
Tangent thermal expansion coefficient × 10 ⁶ , K ⁻¹	1.4	0.8 %
Isothermal secant Compressibility × 10 ⁵ , MPa ⁻¹	0.05	1.2 %
Isothermal tangent Compressibility × 10 ⁵ , MPa ⁻¹	0.05	1.3 %
Entropy, J·K ⁻¹ mol ⁻¹	0.003	— ^a
Enthalpy, kJ·mol ⁻¹	0.001	— ^a
C _p , J·K ⁻¹ mol ⁻¹	0.07	0.3 %
Internal Energy, J·mol ⁻¹	1.1	— ^a
C _v , J·K ⁻¹ mol ⁻¹	0.14	0.6 %

^aNo relative RMS difference is given for the entropy and the enthalpy, because these properties can become zero.

TABLE 21. RMS difference between values on mercury of Vukalovich *et al.* and our recommended values. Ranges 293–323 K and 0–300 MPa

Thermodynamic properties	RMS difference	Relative RMS difference
Density, kg/m ³	0.19	14×10 ⁻⁶
Secant thermal expansion coefficient × 10 ⁶ , K ⁻¹	—	—
Tangent thermal expansion coefficient × 10 ⁶ , K ⁻¹	0.27	0.2 %
Isothermal secant Compressibility × 10 ⁵ , MPa ⁻¹	—	—
Isothermal tangent Compressibility × 10 ⁵ , MPa ⁻¹	0.01	0.3 %
Entropy, J·K ⁻¹ mol ⁻¹	0.007	— ^a
Enthalpy, kJ·mol ⁻¹	0.001	— ^a
C _p , J·K ⁻¹ mol ⁻¹	0.06	0.2 %
Internal Energy, J·mol ⁻¹	—	—
C _v , J·K ⁻¹ mol ⁻¹	0.08	0.3 %

^aNo relative RMS difference is given for the entropy and the enthalpy, because these properties can become zero.

TABLE 22. RMS difference between values on mercury of Kumari and Dass and our recommended values. Ranges 293–323 K and 0–300 MPa

Thermodynamic properties	RMS difference	Relative RMS difference
Density, kg/m^3	0.11	8×10^{-6}
Secant thermal expansion coefficient $\times 10^6$, K^{-1}	0.5	0.3 %
Tangent thermal expansion coefficient $\times 10^6$, K^{-1}	0.2	0.1 %
Isothermal secant Compressibility $\times 10^5$, MPa^{-1}	0.003	0.1 %
Isothermal tangent Compressibility $\times 10^5$, MPa^{-1}	0.01	0.2 %
Entropy, $\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$	0.0005	— ^a
Enthalpy, $\text{kJ}\cdot\text{mol}^{-1}$	0.0002	— ^a
C_p , $\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$	0.01	0.05 %
Internal Energy, $\text{J}\cdot\text{mol}^{-1}$	0.1	— ^a
C_v , $\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$	0.02	0.07 %

^aNo relative RMS difference is given for the entropy and the enthalpy, because these properties can become zero.

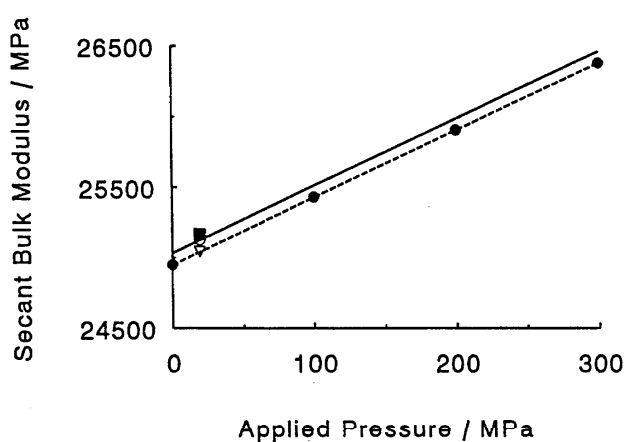


FIG. 1. Isothermal secant bulk modulus at 293.145 K as a function of applied pressure.

● Davis and Gordon⁷ (experimental value);
 ■ Hayward⁸ (experimental value);
 ▽ Davis and Gordon⁷ (interpolated value);
 ○ this paper.

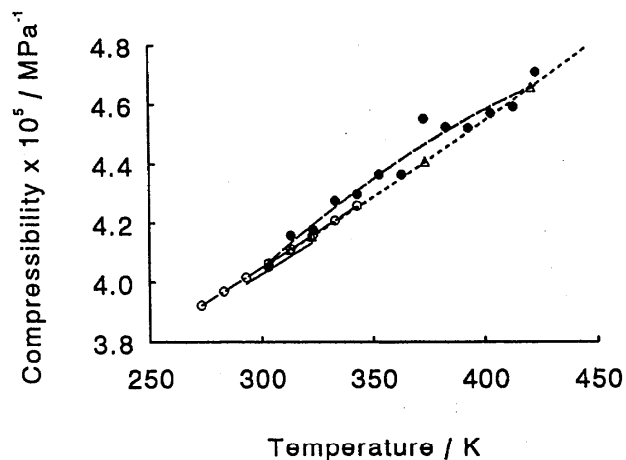


FIG. 2. Isothermal tangent/secant compressibility along an isobar at atmospheric pressure as a function of temperature.

○ Hubbard and Loomis;⁶
 △ Coppens *et al.*;³⁸
 ● Grindley and Lind, Jr.;¹²
 ○ our recommended values.

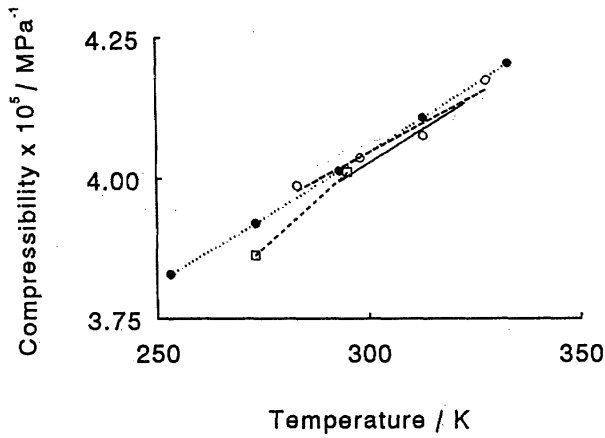


FIG. 3. Isothermal tangent / secant compressibility along an isobar at atmospheric pressure as a function of temperature.
 □ Bridgman (1911)⁷ (a);
 ● Seemann and Klein;³⁶
 ○ Diaz Peña and McGlashan;³²
 — our recommended values.

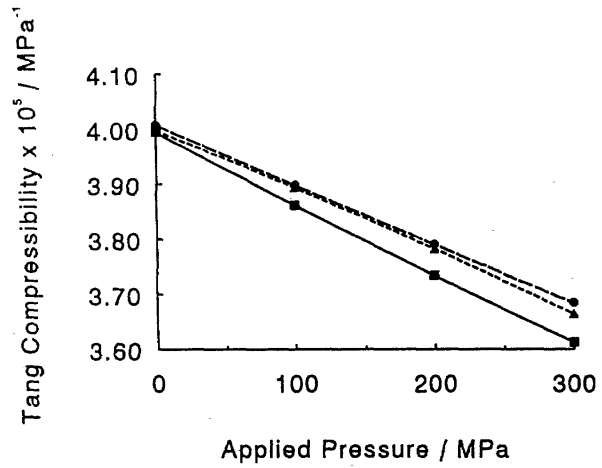


FIG. 5. Isothermal *tangent* compressibility at 293.15 K as a function of applied pressure.
 ▲ Bridgman (1911)⁷ (a);
 ● Grindley and Lind, Jr.¹² (as extrapolated in this paper);
 ■ our recommended values.

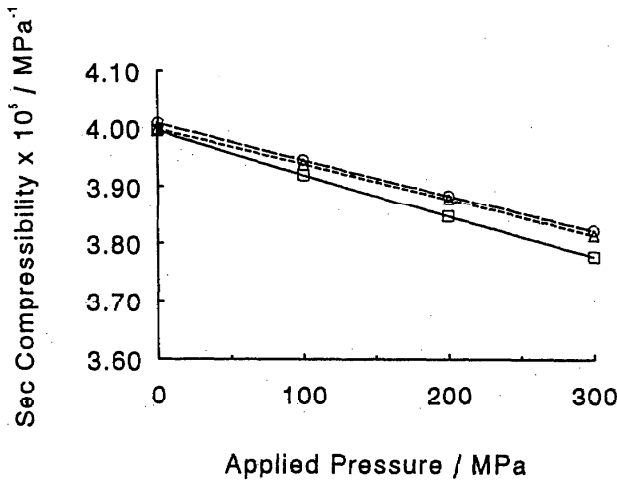


FIG. 4. Isothermal *secant* compressibility at 293.15 K as a function of applied pressure.
 Δ Bridgman (1911)⁷ (a);
 ○ Grindley and Lind, Jr.¹² (as extrapolated in this paper);
 □ our recommended values.

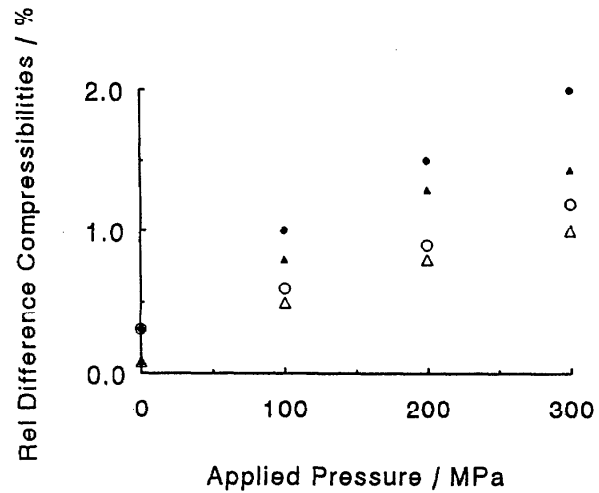


FIG. 6. Relative difference in isothermal secant and tangent compressibility at 293.15 K between Bridgman (1911)⁷ (a), Grindley and Lind, Jr.¹² (as extrapolated in this paper) and our recommended values. The values of Bridgman (1911)⁷ (a), and Grindley and Lind, Jr.¹² are higher than ours.
 Δ secant, ▲ tangent compressibility difference with Bridgman (1911)⁷ (a);
 ○ secant, ● tangent compressibility difference with Grindley and Lind, Jr.¹²

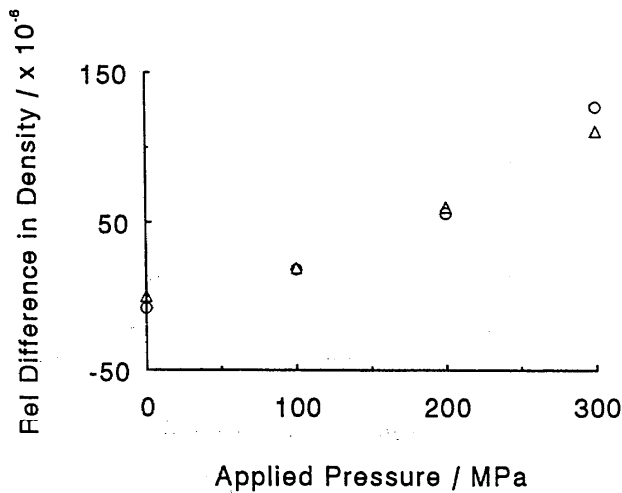


Fig. 7. Relative difference in density at 293.15 K between Bridgman (1911)⁷ (a), Grindley and Lind, Jr.¹² (as extrapolated in this paper), and our recommended values. The values of Bridgman (1911)⁷ (a), and Grindley and Lind, Jr.¹² are higher than ours. Δ relative difference with Bridgman (1911)⁷ (a); \circ relative difference with Grindley and Lind, Jr.¹²

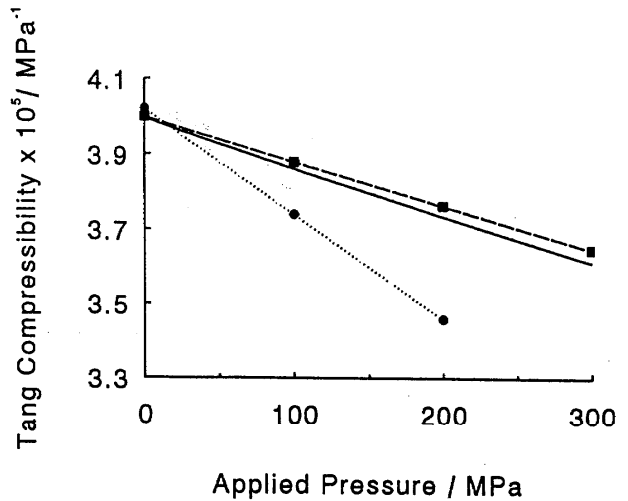


Fig. 9. Isothermal *tangent* compressibility at 293.15 K as a function of applied pressure. \blacksquare Bett, Weale, and Newitt;¹⁰ \bullet Stallard, Rosenbaum, and Davis, Jr.;¹¹ \square our recommended values.

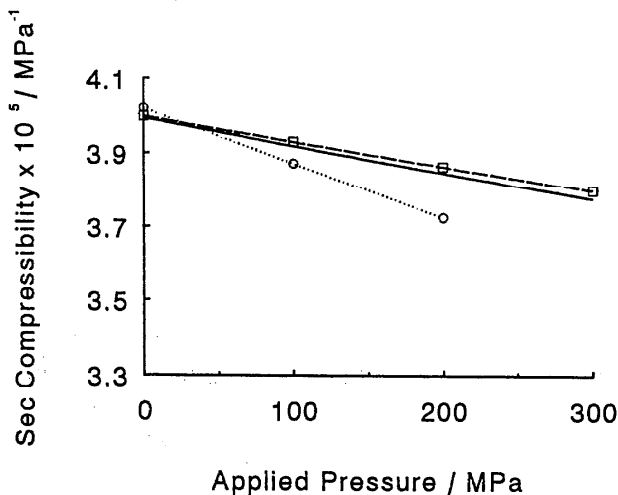


Fig. 8. Isothermal *secant* compressibility at 293.15 K as a function of applied pressure. \square Bett, Weale, and Newitt;¹⁰ \circ Stallard, Rosenbaum, and Davis, Jr.;¹¹ \square our recommended values.

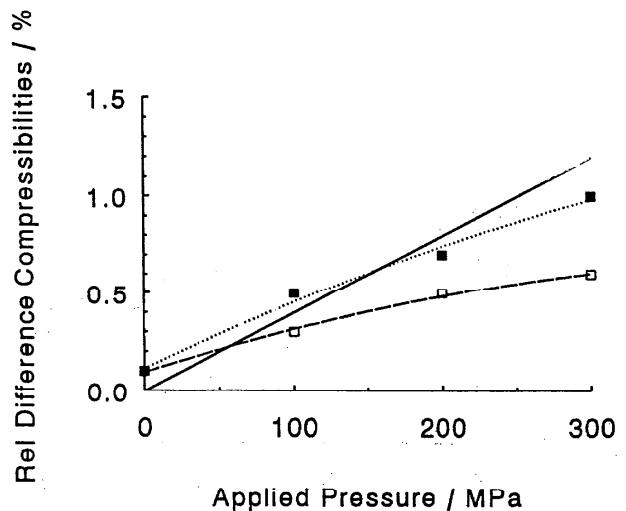


Fig. 10. Relative difference in isothermal secant and tangent compressibility at 293.15 K between Bett, Weale, and Newitt¹⁰ and our recommended values; Bett, Weale, and Newitt's values are higher than ours. \square Relative difference in isothermal secant compressibility; \blacksquare Relative difference in isothermal tangent compressibility. The solid straight line reflects the relative standard deviation, calculated by Bett, Hayes, and Newitt,¹⁰ of the isothermal secant compressibility (by us slightly modified to 293.15 K) as a function of applied pressure; our claimed relative accuracy of the isothermal compressibility in the range 0–300 MPa is about 0.6%. The relative error in the isothermal secant and tangent compressibility have the same value.

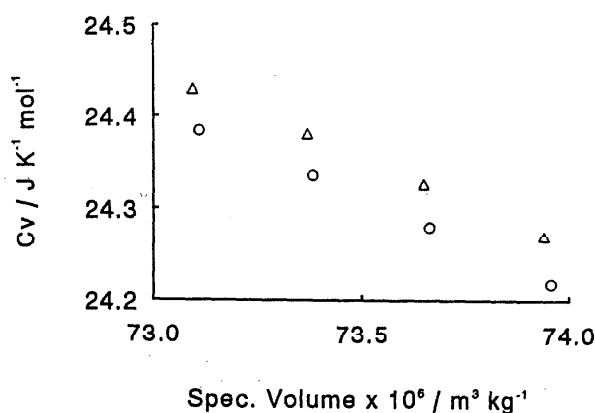


FIG. 11. Isochoric specific heat capacity at 303.15 K as a function of the specific volume from Grindley and Lind, Jr.¹² and our recommended values.

Δ C_v values Grindley and Lind, Jr.¹²;
 \circ C_v recommended values.

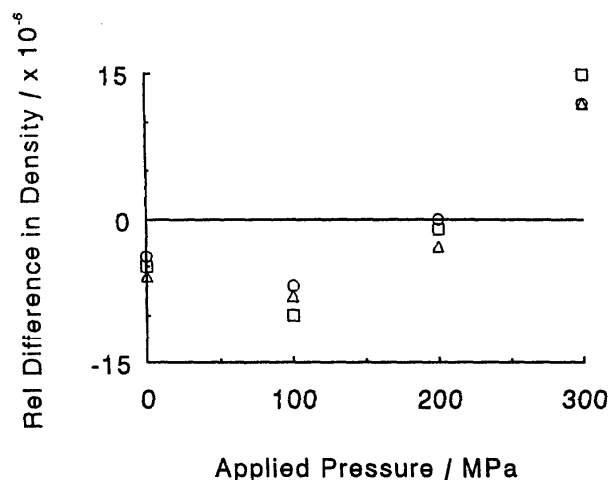


FIG. 12. Relative difference in density at 303.134, 313.130, and 323.127 K between Kumari and Dass,¹⁴ and our recommended values. At 0 MPa applied pressure our recommended values are higher than the values of Kumari and Dass.¹⁴

Δ difference at 303.134 K;
 \circ difference at 313.130 K;
 \square difference at 323.127 K.

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