Mercury-melting-line determination by latent heat method

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The equilibrium pressure for the melting and freezing of mercury was observed for the temperature range −38.834–0.023 °C by latent heat detection. The corresponding pressure range was 0.14–757.32 MPa (MPa = 10^6 N/m^2). The least-squares fit was obtained for this range of pressure with a standard deviation of the residuals of 0.055 MPa for pressure expressed as a third-order polynomial in temperature.

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I. INTRODUCTION

The mercury melting line was recommended as being a "fixed point" on the high-pressure scale by a committee of the Symposium on Accurate Characterization of the High-Pressure Environment.[1] The recommendation of this committee was that the best value of the mercury freezing pressure at 0 °C is 756.9 MPa with an estimated uncertainty of 0.2 MPa. It also suggested that the Simon equation of Bogdanov,[2,3] adjusted to agree with the value of 756.9 MPa at 0 °C, be used.

Since the Gaithersburg meeting, two additional determinations have been made yielding values of 757.1 [4] and 756.9 MPa,[5] respectively, both of which fall within the uncertainty of the recommended value.

Bogdanov[2] estimated the uncertainty of his pressure measurements to be 0.7 MPa at 500 MPa. We estimated that we could determine the melting line at this same pressure with a total systematic uncertainty of 0.1 MPa and with comparable uncertainties at other pressures. Since with these lesser uncertainties the melting line could be more satisfactorily used for calibration purposes, we have made measurements of the melting line in the region of our capabilities. A discussion of uncertainties appears in Sec. IV.

Various means of detecting the mercury melting transition have been used in the past: by volume change,[6] by change of resistance,[7] and by latent heat of fusion.[8] We made an attempt to detect the transition by observing the change in a 10-MHz ultrasonic pulse sent through the walls of a vessel containing the mercury but this method proved to be erratic. A reflected pulse sent in through a buffer rod closure was tried but this also lacked the desired dependability. In the process of these experiments, the magnitude of the change in temperature due to the latent heat became apparent. A vessel including sheathed thermocouples in addition to the platinum resistance thermometer was designed and the latent heat of fusion method became our method of detection.

II. APPARATUS AND TECHNIQUE

The apparatus employed in this work was comprised of a pressure vessel for holding the mercury, a system for subjecting the mercury to a suitable range of pressures, a Manganin resistance gauge for measuring the pressure of the mercury within the vessel, a platinum resistance thermometer for measuring the temperature of the vessel, a thermal control system for regulating the temperature of the pressure vessel, and a differentail thermal sensor for detecting changes in temperature due to the latent heat of fusion of the mercury.

In order to minimize the uncertainty of the temperature measurement, a calibrated platinum resistance thermometer, meeting the defining standards of the International Practical Temperature Scale of 1968 (IPTS 1968), was used to measure the temperature. The resistance of the thermometer was read at the triple point of water and at the equilibrium temperatures of the experiments by a Mueller G-2 dc bridge. The unbalance of the bridge was amplified and fed to a dual-channel strip-chart recorder. The sensitivity of the system was such that resistance changes equivalent to 0.001 °C could be measured. The estimated systematic uncertainty of the temperature measurement was 0.002 °C. The pressure vessel shown in Fig. 1 was constructed of maraging steel with a well for the standard platinum resistance thermometer, a well for a sheathed chromel-alumel thermocouple, and a through hole for the mercury. The lower end of the through hole was closed with a solid plug and the upper end was connected to high-pressure tubing through which a sheathed thermocouple extended down into the mercury. A mixture of *n*-pentane and *i*-pentane was used as the pressure fluid. The high-pressure tubing supported the pressure vessel and thermometer in a temperature-controlled bath shown in Fig. 2. The high-pressure tubing extended above the bath to a tee through which the sheathed thermocouple exited the pressure system. The stainless-steel sheath of this thermocouple was

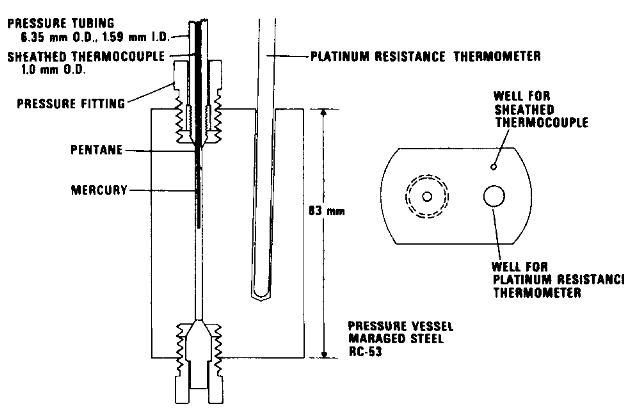

FIG. 1. Detailed drawing of pressure vessel, showing a vertical cross section and a top view.

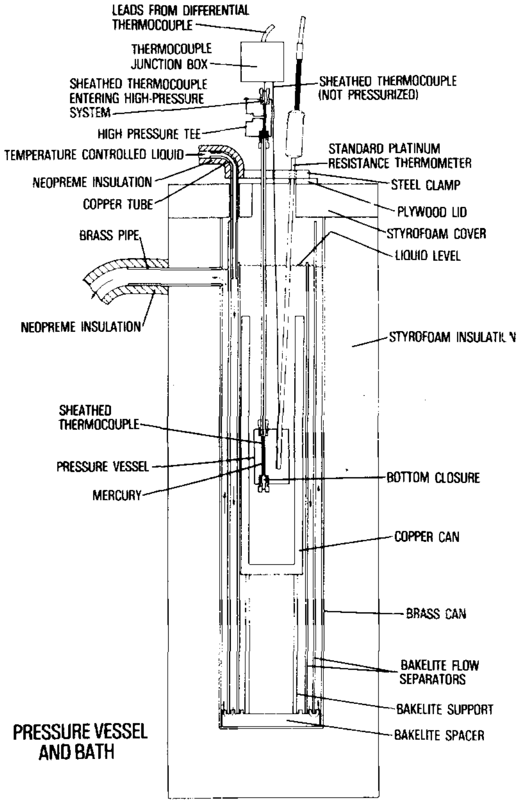

FIG. 2. Pressure vessel and bath.

silver soldered into a plug which sealed the top part of the tee. Pressure was applied through the side port of the tee. The pressure was generated by an intensifier with primary oil pressure supplied by an air-driven pump with a screw-driven hand generator in parallel for semifine adjustment. The high-pressure side of the intensifier was precharged with the pentane mixture by a hand pump, which was then valved off. Another valve in the high-pressure system was turned in and out to vary the volume and provided the fine pressure control. The two sheathed thermocouples, one from the mercury and the second from the well, entered an aluminum box mounted above the tee, where two similar wires were connected together, and leads attached to the other two wires were led out for connection to an amplifier. The output was therefore a measure of the difference in temperature between the mercury and the pressure vessel. The aluminum box served as a thermal shield to provide uniform temperature for these junctions. The amplified signal was fed into one channel of the dual-channel strip-chart recorder. The noise of the system was such that changes of 0.002 °C could be seen.

Two insulated baths were used for the temperature-control system. A mechanically refrigerated bath was filled with alcohol, which was pumped to the bath holding the pressure vessel. The alcohol then returned to the first bath by gravity. The first bath, which contained the pump, was continually cooled by the refrigerator and the temperature of the alcohol leaving the pump was monitored by the platinum resistance element of a controller which supplied electric power to a heater in this bath to maintain the set temperature. This fluid varied in temperature by up to 0.010 °C. The second bath was lagged to eliminate this variation by having the pressure vessel inside a heavy copper can filled with stagnant alcohol, which in turn was surrounded by two concentric Bakelite tubes, the inner one serving to further lag the temperature. The temperature-controlled alcohol, after flowing down around the outside of the inner tube and up around the outside of the second tube, was returned to the first bath. This lagging reduced the fluctuations and gave temperatures stable to 1 mdeg/h after equilibrium. The liquid mercury was usually superpressurized by between 55 and 100 MPa before it froze. When it freezes under these conditions, the pressure is valueless as a freezing point determination and the latent heat raises the temperature of the pressure vessel and the surrounding bath, requiring several hours to return to equilibrium conditions. Two different pressure vessels were used, the first with a bore of 4.8 mm for pressures to 420 MPa and the second with a bore of 2.3 mm for pressures to 757 MPa. The larger amount of mercury used in the first vessel caused a rise in the temperature of the vessel, from 0.125 to 0.160 °C on freezing, whereas the smaller amount in the second vessel caused the 0.060–0.075 °C rise. The second vessel was used to determine maximum temperature differences between the mercury and the vessel and showed brief differences of 0.8–1.8 °C on the freezing from the supercooled state and approximately a 0.4 °C difference on the melting due to a fairly large pressure decrease. Figure 3 shows a temporal trace from a dual-channel recorder of temperature changes on superpressurized freezing on complete rapid melting of the mercury sample and on superpressurized freezing. The right-hand trace shows the amplified unbalance form the Mueller bridge, normally balanced to determine the temperature of the vessel. This shows changes in temperature of 0.060 °C for both freezing and melting. The left-hand trace shows the amplified signal from the sheathed differential thermocouples, one junction in the mercury, the other in a well in the vessel. On freezing by superpressurization, the quick freezing results in an increase in the tem-

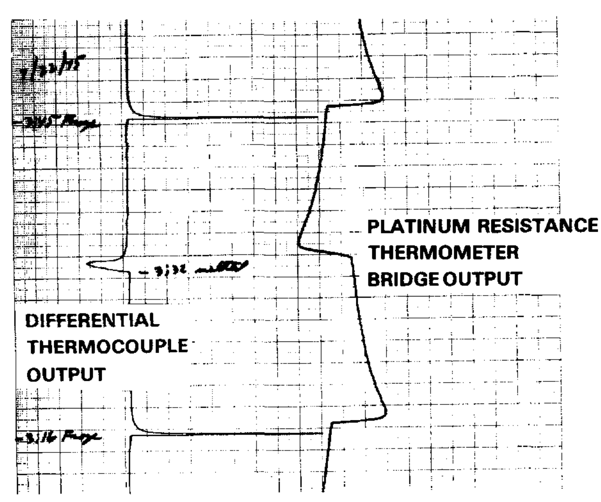

FIG. 3. Temperature changes on superpressurized freezing and on complete rapid melting of the mercury sample.

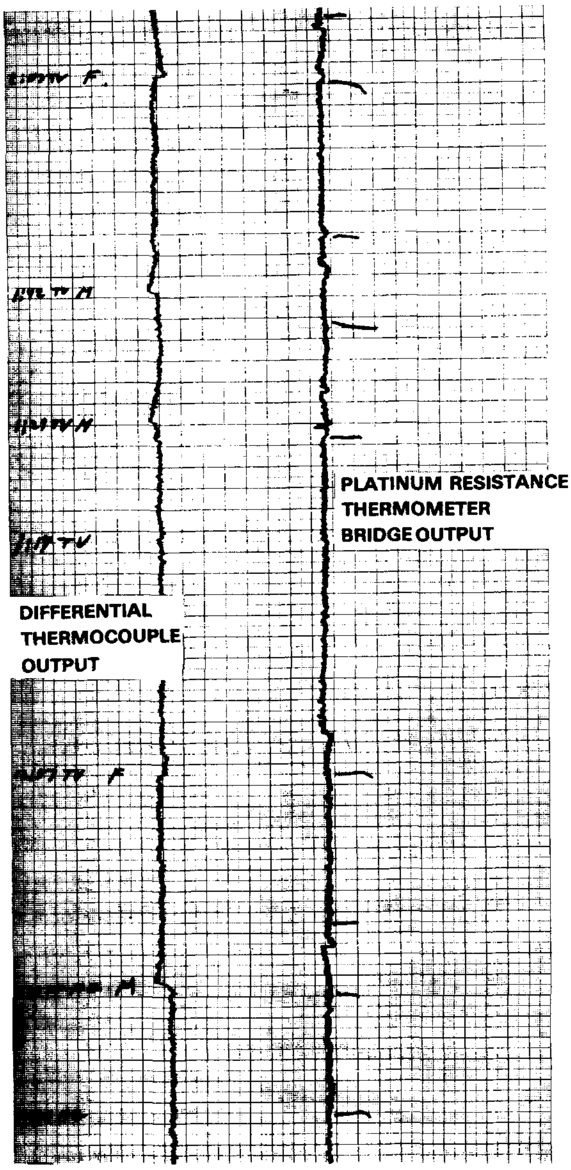

FIG. 4. Recordings of temperature changes during the melting-line determination.

perature of the mercury of 1.8 °C. On melting by reducing the pressure, a decrease in temperature of 0.4 °C is shown covering a longer period of time.

III. PROCEDURE

For detection of the phase transition, the bath is set for the desired temperature, the mercury is overpressurized to cause it to freeze, and sufficient time is allowed for the system to come to equilibrium. The recorder is set for greater sensitivity than that shown in Fig. 3. The recorder sensitivity for the bridge output is 4 mm/0.001 °C and the bridge is kept manually balanced to read temperatures of the vessel to 0.001 °C. The recorder sensitivity of the output from the differential thermocouple is 1 mm/0.001 °C and changes of approximately 0.002 °C can be seen above the noise level. The pressure is then decreased to near the expected pressure for phase transition, then it is further decreased by increments of about 0.1 MPa every 10 min.

Figure 4 shows the recorder traces for several pressure adjustments to cause melting and freezing during an elapsed time of almost 2 h. The left-hand trace (the differential thermocouple output) shows the melting (M) or freezing (F) occurring when the pressure is changed either by operating a hand generator (HG) on the low-pressure side of the intensifier for coarse pressure changes or by turning a valve (TV) in the high-pressure system which changed the pressure by changing the volume of the system by the travel of the valve. The right-hand trace was used to monitor the output of the bridge for measuring the resistance of the platinum resistance thermometer and the tick marks indicate places where the current was reversed after balancing the bridge.

The pressure was determined by measuring the resistance of a seasoned calibrated four-lead Manganin coil with a Mueller bridge. (This Manganin coil had been calibrated against a controlled clearance piston gauge which had an upper limt of 420 MPa and an estimated systematic uncertainty of 100 ppm. Thirty points were used in the calibration over the range of pressure 0—420 MPa and a least-squares fit was obtained for pressure as a second-order polynomial of resistance of the Manganin gauge with a residual standard deviation

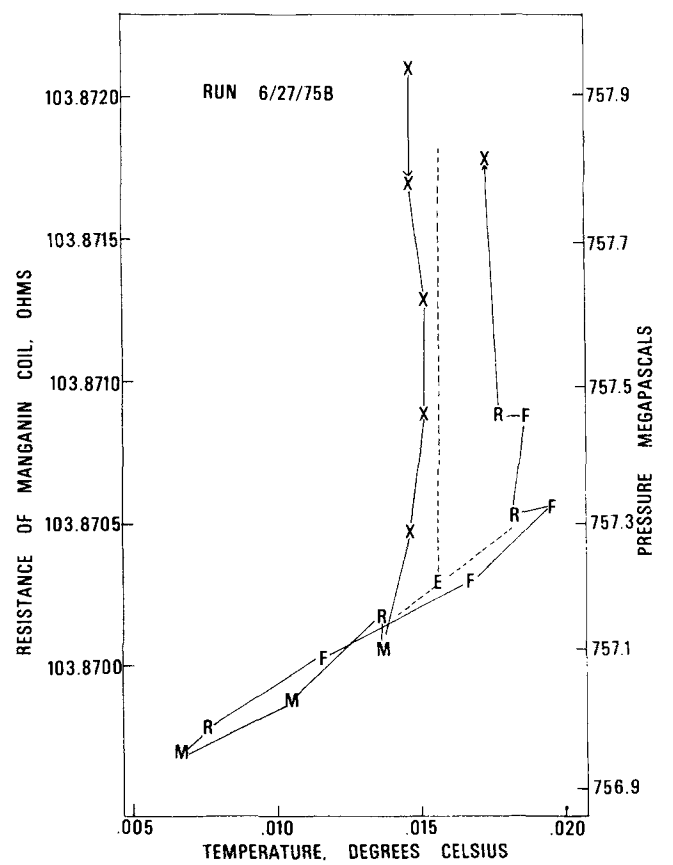

FIG. 5. Plot of melting and freezing to determine a single point on the melting line [temperature of pressure vessel after changes in pressure: X—change in pressure, no apparent melting or freezing; M(F)—melting (freezing) observed by differential thermocouple; R—recovery after melting or freezing; E—graphically estimated value for melting-freezing pressure at equilibrium temperature of the system].

TABLE I. Mercury-melting-line data in order of acquisition.

Pressure (MPa)	Temperature (K)	Pressure (MPa)	Temperature (K)
183.32	243.784	110.16	240.001
235.84	246.496	54.41	237.119
235.86	246.498	54.20	237.109
183.50	243.795	5.35	234.588
235.85	246.495	5.46	234.592
235.91	246.499	5.56	234.593
235.26	246.461	30.47	235.884
288.50	249.205	30.52	235.887
341.34	251.925	613.36	265.856
394.43	254.657	613.03	265.836
182.79	243.752	654.07	267.930
394.28	254.642	676.00	269.048
288.56	249.205	679.70	269.237
394.28	254.649	757.28	273.170
288.08	249.184	757.32	273.173
393.98	254.633	757.15	273.161
446.86	257.348	757.20	273.166
446.84	257.346	237.74	246.588
500.24	260.073	237.76	246.586
394.12	254.632	0.16	234.316
288.12	249.190	0.27	234.323
500.02	260.067	0.34	234.326
533.96	261.801	0.14	234.316
144.78	241.793	0.20	234.319
144.82	241.796	0.19	234.318
110.04	239.996	0.18	234.317

of 0.025 MPa.) The pressure obtained from the resistance of the Manganin gauge (using an extrapolation of the calibration equation) and the temperature obtained from the platinum resistance thermometer for a number of points from one run were plotted as shown in Fig. 5. The intersection of the melting line with the estimated equilibrium temperature was used as a single point for use in calculating the mercury freezing line. Forty-five such determinations were made covering the pressure range 5.35—757.32 MPa. A least-squares fit these 45 mercury melting pressures was obtained as a third-order polynomial in temperature. This equation gave a value at 0 °C which was 0.06 MPa below the suggested value of 756.9 MPa. This is well within the stated uncertainty of the value but is in no way to be considered as a redetermination of the 0 °C freezing pressure value. A redetermination of this value may be undertaken when our next controlled clearance piston gauge (800 MPa) is in operation. For purposes of this present determination of the melting and freezing line, the four points obtained near 0 °C were assigned pressure values (corrected for small temperature differences) based on the recommended value of 756.9 MPa. These four assigned pressures and the measured resistance of the Manganin coil at these experimental points were added as pressure calibration points to the 30 original points obtained using the controlled clearance piston gauge and a least-squares fit was again obtained for pressure as a second-order polynomial of resistance of the Manganin gauge. This fit had a residual standard deviation of 0.027 MPa. The pressure given by this equation at 420 MPa is 0.012 MPa above the original calibration equation. This calibration equation was then used to recalculate the pressures for the experimental points for the mercury melting lines and therefore adjusts the mercury-melting-line equation to the value 756.9 MPa at 0 °C.

As a check on the assumption that the equilibrium temperature was that indicated by the platinum resistance thermometer at a low temperature and that temperature gradients had not been overlooked, freezing point determinations near atmospheric pressure were made. The same high-pressure vessel was left in place in the bath, the temperature was taken slightly below the freezing point temperature, and the system was overpressurized to freeze the mercury. The pressure was then reduced to atmospheric pressure and a calibrated low-pressure bourdon-tube gauge was connected to the system. The pressure was increased by a hand pump to about 0.15 MPa and thermostat was set to slowly raise the temperature of the bath. While the temperature was monitored, the pressure was reduced to atmospheric, then raised again observing the differential thermocouple output to detect melting or freezing. Values of pressure and temperature for melting and freezing were obtained for pressures 0.14—0.34 MPa. Two such runs (consisting of a total of seven points) were made and the points obtained were fitted to a linear equation and extrapolated to atmospheric pressure. The temperature obtained for freezing at atmospheric pressure was −38.836 °C. This is in agreement with the same value −38.836 °C for the atmospheric freezing pressure of mercury calculated from the triple-point temperature −38.841 °C determined by Furukawa (Thermometry Section, Heat Division, Institute for Basic Standards). This agreement serves as a check on the calibration of the platinum resistance thermometer and the lack of gradients at equilibrium. These seven points were added to the 45 points obtained using the Manganin gauge to give 52 points for the calculation of the mercury melting line.

IV. RESULTS

The pressure and temperature for the 52 points, obtained as previously described, are given in Table I.

Bogdanov's Simon equation had been modified by the committee[1] to pass through 756.9 MPa at 0 °C. We further modified it by changing the coefficient again to still pass through 756.9 MPa at 0 °C for a triple-point temperature of 234.309 K for use with temperature measured on the IPTS 1968 scale. This modified equation

$$P=3824.91\left[\left(\frac{T}{234.309}\right)^{1.1772}-1\right], \qquad (1)$$

where T is the Kelvin ($T=273.15+t$ °C) and P is in MPa, was used to calculate the pressure from the temperature of each of the experimental points. The difference between these calculated pressures and the experimental pressures ranged from −0.030 to +0.757 MPa. This is close to the estimated uncertainty stated by Bogdanov[2] of 0.7 MPa at 500 MPa.

Since for this limited pressure range and with these arbitrary modifications this equation no longer appeared to be a good fit to the data, we determined a two-parameter Simon equation under the same constraints and obtained an exponent of 1.1346 by a least-

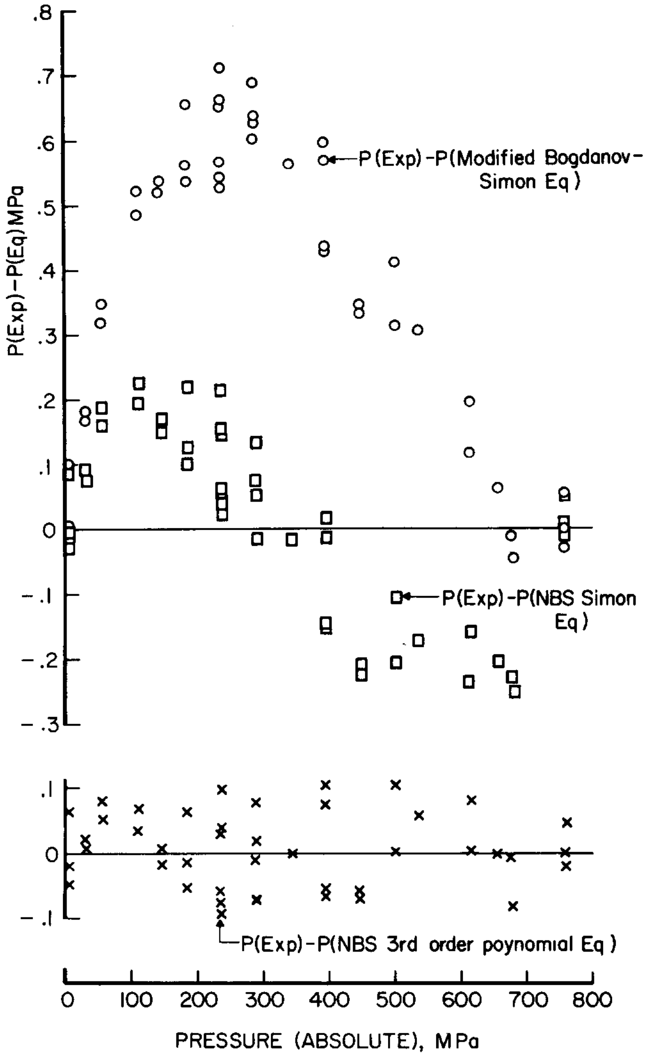

FIG. 6. Residuals from fitting three different functions of temperature to the data.

squares method to give

$$P=3981.89\left[\left(\frac{T}{234.309}\right)^{1.1346}-1\right], \qquad (2)$$

where T is in Kelvin and P is in MPa. The differences between pressures calculated from this equation and the experimental pressures ranged from -0.262 to 0.230 MPa. The residuals for both Eqs. (1) and (2) are plotted in Fig. 6. From this it is seen that there are systematic deviations for both equations. It appears that a two-parameter Simon equation is not the best choice for the mercury melting line. Hardy, Crawford, and Daniels[9] concluded that argon and mercury melting lines could not *both* be fitted by the two-parameter Simon equations.

We fitted a third-order polynomial to the data and obtained the following equation:

$$P=19.33115d+0.0014055d^2+0.000067028d^3, \qquad (3)$$

where P is in MPa and $d=T-234.309$ K. The pressure at 234.309 K, the triple point of mercury, is approximately 0.0002 Pa, which is sufficiently close to zero to be set to zero in these equations. The deviations from this curve ranged from -0.096 to $+0.104$ MPa with the residual standard deviation from the curve equal to 0.055 MPa. These deviations are also shown in Fig. 6. There is no significant systematic variation of the residuals from Eq. (3). That fact and the smaller size of the deviations show this to be the most satisfactory equation to use over the range of pressure 0–757 MPa.

At 420 MPa (the highest pressure at which the controlled clearance piston gauge was used) the estimated systematic uncertainties total 0.09 MPa with 0.04 MPa from the original pressure calibration, 0.01 MPa from the small modification of the calibration due to including the 757-MPa points, and 0.04 MPa from the temperature uncertainty. The residual standard deviation from Eq. (3) is 0.055 MPa and σ (the standard deviation of the predicted value) at 420 MPa is 0.014 MPa; 3σ plus the estimated systematic uncertainties give a total uncertainty of 0.14 MPa. This total uncertainty would be slightly smaller below 420 MPa and increase at higher pressures. At 757 MPa, σ is 0.025 MPa, while the controlling uncertainty is the 0.2 MPa stated uncertainty.[1]

Equation (3) should serve as a calibration equation over the range 0–757 MPa until some new value of the freezing pressure of mercury at 0 °C is defined.

[1]Committee report on fixed points near room temperature, *Proceedings of the Symposium on Accurate Characterization of the High-Pressure Environment*, NBS Spec. Publ. 326 (National Bureau of Standards, Washington, D.C., 1971), p. 313.
[2]V.S. Bogdanov, Yu.L. Levin, S.S. Sekoyan, and Yu.I. Schmin, in Ref. 1, p. 297.
[3]V.S. Bogdanov, Izmeritel'naya Tecknika (No. 8), 29 (1967).
[4]A.L. Ruoff, R.C. Lincoln, and Y.C. Chen, J. Phys. D **6**, 1295 (1973).
[5]S. Yamamoto, *Proceedings of the 4th International Conference on High Pressure* (Physico-Chemical Soc. of Japan, Kyoto, 1975), p. 810.
[6]D.H. Newhall, L.H. Abott, and R.A. Dunn, *High Pressure Measurement*, edited by A.A. Giardini and E.C. Lloyd (Butterworths, Washington, 1963), p. 339.
[7]R.S. Dadson and R.G.P. Greig, Br. J. Appl. Phys. **16**, 1711 (1965).
[8]A.R. Beavitt, J. Phys. E 2, 841 (1969).
[9]W.H. Hardy, R.K. Crawford, and W.B. Daniels, J. Chem. Phys. **54**, 1005 (1971).