at the ice point. The ice-water mixture was contained in a Dewar flask, which in turn was enclosed in a thermally insulated container. The temperature of the bath was checked periodically by a platinum resistance thermometer and was found to remain constant within ± 0.002 °C. The interior of the pressure vessel exceeded the temperature of the bath by about 0.005 °C.

In the range of the transition the pressure was changed in increments of 0.1 bar (contrast with bismuth and barium). Changes of this magnitude on either side of the equilibrium point were found to give almost instantaneously a recognizable drift in electrical resistance. The mean value of a series of 74 measurements is 7.5692 kbar. The dispersion of the data is reproduced in a histogram and appears to be distributed normally about the mean. The total uncertainty is reported as ± 1.2 bar.

A report of a determination of the mercury point has recently been published by K. Yasunami (1967 a, b). He used a lever-type controlled-clearance gage and detected the freezing pressure of mercury by a latent-heat detector. This detector was constructed of 16 pairs of semiconductor thermal elements having a sensitivity of 400 μV/°C/pair. Temperature was controlled to ± 0.001 °C. The use of the lever-type piston gage allows the use of a piston whose area is one cm^2, which is 15.5 times the area of pistons used by other investigators. Yasunami reports the value of 7.5710 kbar ± 1.2 bar within 99.7 percent statistical confidance limits.

All the recent studies of the mercury transition include excellent discussions of the sources of error. The 'best value' selected for the mercury transition pressure at 0 °C is 7.5692 kbar ± 1.5 bar. The 7.5692 value is based upon a weighted average of all the data of table 3, and the 1.5 bar error represents the rms deviation from the average of all the weighted values (except that of Bridgman, whose value is definitely low.)

TABLE 3. Mercury (liquid $-\alpha$) at 0 °C

Researcher	Transition pressure (kbar)	Error (bar)	Method of detection
Bridgman (1911b) [a]	7.492	72	Volume
Johnson and Newhall (1953)	7.568	50	Volume
Zhokhovskii (1955)	7.5658	3	Pressure drop as transition initiates
Zhokhovskii, Razuminkhin, Zolotykh, Burova (1959)	7.5697	23	
Newhall, Abbot, and Dunn (1963)	7.5662	3.4	Volume
Dadson and Greig (1965) [b]	7.5692	1.2	Electrical resistance
Yasunami (1967a, 1968) [c]	7.5710	1.2	Latent heat
Cross (1968)	7.5674	1.6	Electrical resistance
Best Value (Weighted Average) [d]	7.5692	1.5 [e]	

[a] This value is the average of two volume and four electrical resistance determinations.
[b] 74 experimental determinations.
[c] 16 experimental determinations.
[d] Each value is weighted proportional to 1/(Error)^2.
[e] RMS deviation of weighted values (excluding Bridgman's).

b. Bismuth I–II

Three polymorphic transitions occur in bismuth at room temperatures, two of which are important pressure-calibration points (i.e., Bi I–II, Bi III–V). The Bi II–III transition, being so close to the Bi I–II point, is of little value as an additional calibration point.

At the time Bridgman began making compressibility measurements in the 30 kbar region, he felt that more precise measurements were desirable. As to his approach he states: "One would naturally first try to merely extend the former procedure to higher pressure, but this is not feasible because the free piston had about reached its limit at 13,000 due to rapidly increasing viscosity of the pressure-transmitting medium, demanding forces to rotate the piston great enough to break it, and also due to the rapidly increasing distortion, the correction for which can only be calculated by the methods of the theory of elasticity in a range in which the fundamental assumptions of the theory are becoming rapidly inapplicable. However, the fundamental idea of the free-piston gage, namely, the measurement of pressure by measurement of the thrust on a piston in equilibrium with the pressure, appears to remain the simplest and perhaps the only method. The errors to which this is subject are two: those arising from friction and those arising from geometrical distortion. If these two sources of error could be overcome, then an extension of the same procedure as before could be used, namely, direct measurement of some easily determined pressure fixed point against which the manganin gage could then be calibrated and used thereafter as a secondary gage" (Bridgman, 1940b).

Using the approach mentioned and taking into account corrections for friction and distortion of the apparatus, Bridgman experimentally determined the pressure of the solid-solid Bi I–II transition. The value reported for the transition was 25,420 kg/cm^2 (24.930 kbar) at 30°C, which can be transferred for comparison to 25.155 kbar at 25 °C using the later measured slope of the phase line. With the transition pressure of the bismuth point and mercury point known, manganin wire gages were calibrated in terms of both. These experiments were carried out in liquid systems and yielded a workable calibration scale up to 30 kbar.

A great deal of experimental work has been done on the re-examination of the Bi I–II transition and other fixed points of interest to the calibration of high-pressure apparatus. Babb (1963) published a correction to Bridgman's 30-kbar pressure scale on the basis of the new determination of the freezing point of mercury at 0 °C by Dadson and Greig. Included with this work was a corrected value of 25.375 kbar for the Bi I–II transition at 25 °C.

Boyd and England (1960), using a simple piston-cylinder apparatus which they describe as based on the Coes-Hall design, arrived at the value 25.200 ± 0.4 kbar at 30 °C. The hysteresis of the electrical trace was 11.6 percent. "By balancing on the transition with phases I and II present, increasing the pressure until I → II and releasing the pressure until II → I, it was possible to reduce the hysteresis to 3.1 percent about a mean value of 25.2 kbar." The 25.2 value at 30 °C corresponds to 25.4 kbar at 25 °C.

Kennedy and LaMori published two papers (1961, 1962) in which they employed a piston-cylinder (not a free-piston gage) with a solid-media sample chamber and measured the Bi I–II transition. They rotated the piston through an angle of a few degrees at each pressure to reduce frictional effects in the piston device on the up and down stroke. They reported a value of 25.380 ± 0.020 kbar at 20 °C in their 1962 paper. The error flag in this work represented a repeatability flag and did not include any systematic error analysis. The pressure corresponding to the midpoint of the interval between the up and down stroke was selected as the equilibrium pressure. Since both nucleation hysteresis and the "region of indifference" growth hysteresis, as well as the apparatus frictional effects, are all undetermined in this experiment, the absolute uncertainty is obviously much greater than 20 bar. Heydemann (1967a) has estimated an uncertainty of approximately ± 175 bar for the Kennedy-LaMori measurement, which estimate is smaller than the concensus of the present reviewers.

Vereshchagin, et al. (1966) published the value of 25.4 kbar ± 0.1 percent for the Bi I–II transition pressure but gave insufficient details to make an evaluation of their work possible.

Johnson and Heydemann (1967) describe a dead weight, free-piston gage with a range up to 26 kbar (see section 2). Using this apparatus Heydemann (1967a) published the results of determinations of the Bi I–II transition pressure on samples of two different purities. This measurement was carried out in a true hydrostatic medium where nucleation and growth rate effects could be studied, which allows a much more meaningful statement of thermodynamic equilibrium to be made. Correction errors due to friction are also virtually eliminated. With a bismuth sample purity of 99.999 percent the transition pressure was 25.499 ± 0.060 kbar and for 99.8 percent pure bismuth a pressure of 25.481 ± 0.060 kbar was determined.

The determinations discussed above are given in table 4 for quick reference. Two shock measurements are also presented for interest, one by Duff and Minshall (1957) and one by Larsen (1967). The shock measurements are not directly comparable due to nucleation and other sample hysteresis and non-equilibrium effects. By the very nature of the measurement techniques used in the determinations shown, the measurement of Heydemann (1967a) uniquely meets the requirements for a standardization measurement of a fixed point since only this measurement is referred to the primary free-piston gage. For this reason we have selected as a best value for the Bi I–II equilibrium transition pressure the value 25.499 ± 0.060 kbar reported by Heydemann.

It is of interest to note from table 4 that the average of all the values except Heydemann's centers around 25.4 kbar or approximately 100 bar below Heydemann's value and outside his error flag. Although this may be simply statistical error in the previous measurements, all of which have error flags greater than 100 bar, there is an explanation for this effect. Zeto, et al. (1968)

TABLE 4. Bismuth I–II transition at 25 °C

Researcher	Transition pressure (kbar)	Error (kbar)	Method of detection	Sample purity
Bridgman (1940a) [a]	(e) 25.155		Volume	
Duff and Minshall (1957)	(s) 25.580	0.13	Shock	
Boyd and England (1960) [a]	(a) 25.400	.4	Volume	99.99% Electrolytic Bi
Kennedy and LaMori (1961)	(a) 25.410	See text	Volume	99.999%
Kennedy and LaMori (1962)	(a) 25.380	See text	Volume	
Babb (1963) (correction of Bridgman)	(e) 25.375		Correction	
Heydemann (1967)	(e) 25.499	.060	Volume	99.999%
	(e) 25.481	.060		99.8%
Vereshchagin, et al. (1966)	25.4	.25		
Larsen (1967)	(s) 25.4	.8	Shock	
Best Value [b]	25.499	.060		

(e) equilibrium; (s) shock; (a) average of increasing and decreasing cycle.
[a] Measurement made at 30 °C.
[b] Heydemann's (1967) value accepted (see text).