it was demonstrated that Bridgman's (1952) electrical resistance transition of 54 kbar is the same one that he observed at 44 kbar by volume methods.

Kennedy and LaMori (1961, 1962) reported a pressure of 41.8 ± 1 kbar for the Cs II–IV transitions using volume-type measurements. The uncertainty here should undoubtedly be enlarged since the investigators were not even aware of the two closely spaced transitions and did not observe them. On the compression cycle the initiation pressure of the Cs II–III point was measured, while on the decompression cycle the initiation pressure of the Cs IV–III point was measured. Considering the fact that the range of existence of Cs III is about 0.5 kbar wide at 25 °C, a better value for the Cs II–III equilibrium transition pressure is 41.5 ± 1.2 kbar using the Kennedy and LaMori data. This value places the Cs III–IV transition pressure at 42.0 ± 1.2 kbar, indicating an increase in the observed hysteresis by 0.5 kbar, and increases the uncertainty slightly.

At the present time not enough work has been done on the calibration of the cesium transition to recommend a best value. It appears that either the Cs II–III or Cs III–IV point might serve as a better calibration point than the Tl II–III points as they exhibit much less nucleation hysteresis and are very nearly midway between the Bi I–II and Ba I–II points. The chief disadvantage of using cesium for calibration is its high chemical activity. This can be overcome by careful handling procedures, but it is generally difficult to maintain a high purity.

c. Barium I–II

Bridgman (1941, 1942) in his volumetric studies reported two transitions in Ba, one at approximately 17 kbar and one at 60,000 kg/cm² (59 kbar). These became known as the Ba I–II and the Ba II–IV, respectively. In 1952 he located an electrical resistance discontinuity which he placed at 80,000 kg/cm² (78 kbar). Bridgman suggested that this transition may be associated with the former one at 59 kbar. The fact that these are actually the same transition was suggested by Kennedy and LaMori (1961) and was later proved by Barnett, Bennion, and Hall (1963) using simultaneous x-ray and electrical resistance measurements. No workers other than Bridgman ever observed the transition at 17 kbar, and its existence is uncertain. Bridgman's 59 kbar transition is presently referred to as the Ba I–II transition. The accurate determination of this point is of prime importance in high-pressure calibration since all extrapolation procedures to higher pressures depend strongly upon it. Kennedy and LaMori (1962) in the first calibration-type measurement obtained a preliminary value of 59.6 kbar from a single experiment during which a piston broke at the initiation of the transition. Later LaMori (1963) published the value of 59.1 ± 1.6 kbar using a double stage piston-cylinder device in which the polymorphic transi-

TABLE 6. Cesium transitions

Researcher	Transition pressure (kbar)	Error (kbar)	Temp.	Method of detection
		Cesium I–II		
Bridgman (1938a)	(e) 21.63		30 °C	Electrical resistance
	(e) 21.59		25 °C	
Bridgman (1938b)	(e) 23.0		Room temp.	Volume
Kennedy and LaMori (1962)	(e) 22.6	0.6	25 °C	Volume
		Cesium II–IV		
Bridgman (1948)	44		10 °C	Volume
Bridgman (1952)	(c) 54			Electrical resistance
Kennedy and LaMori (1961)	(e) 41.8	1	Room temp.	Volume
Kennedy and LaMori (1962)	(e) 41.725	1	Room temp.	Volume
		Cesium II–III		
Revised (1967)[a]	41.5	1.2	25 °C	Calculations
		Cesium III–IV		
Revised (1967)[a]	42.0	1.2	25 °C	Calculations

(e) equilibrium; (c) compression.

[a] Transition pressure calculated from data of Kennedy and LaMori (1962) using data of Hall, Merrill, and Barnett showing the existence of two separate closely spaced transitions.

Highest sample purity stated in any of the above experiments was 99 percent.

tion was detected by the electrical resistance discontinuity. A very large hysteresis was reported. On compression the transition initiated at 67.4±0.6 kbar and on release at 54.4±0.6 kbar resulting in an overall hysteresis of 13 kbar. With a hysteresis of this magnitude, the assumption that the friction of the up and down stroke is symmetrical about the equilibrium pressure is not necessarily valid.

Using the lattice constant of NaCl as a pressure gage and referring to the semi-empirical equation of state of Decker (1965), Jeffery, et al. (1966) reported a value of 53.3±1.2 kbar for the equilibrium pressure of the Ba I–II transition. Later improvement of the input data for Decker's theory (1971) coupled with the NaCl compression data of Jeffery, et al., yield an improved equilibrium pressure of 54.7 kbar for this barium transition.

The pressure of the Ba I–II transition has been determined to be 55.0±0.5 kbar at 22 °C by Haygarth, Getting, and Kennedy (1967) using a "modified single-stage piston-cylinder apparatus". These investigators used a piston whose unconstrained length to diameter ratio was less than unity. Under such a condition the compressive strength of the tungsten carbide piston increases and extends the pressure range of the piston-cylinder apparatus. The barium sample was in the form of a strip confined in a AgCl or AgBr pressure medium. The transition was detected by electrical resistance measurements. Samples of three purities were used indicating a small but detectable effect upon the transition point. The average transition pressures for the three different purities are given below:

Purity	Transition pressure	Average hysteresis	Number of determinations
99.5%	54.7 ± 0.5 kbar	5.6 kbar	11
High Purity 1	54.9 ± 0.5 kbar	5.1 kbar	1
High Purity 2	55.0 ± 0.5 kbar	5.7 kbar	6

Zeto, et al. (1968) made a determination of the Ba I–II point in a hydrostatic environment. The pressure-transmitting fluid was a 50–50 mixture by volume of pentane and iso-pentane, whose hydrostaticity at that pressure was demonstrated by viscosity measurements (Barnett and Bosco, 1969). The pressure calibration is based upon the extrapolation of the relative resistance change of a manganin gage by means of a quadratic equation whose coefficients are determined by a two-point calibration at the Hg L–I at room temperature and the Bi I–II transition. The equilibrium transition pressure was taken as the center of the region of indifference and is reported at 56.27 kbar.

The "best value" for the barium transition pressure is based on an average of the published values of Jeffery et al. (1966; Decker, 1968), Haygarth et al. (1967), and Zeto and Vanfleet (1969). The low-purity value of Haygarth is used since 99.5 percent purity is the material readily available and generally used. The errors discussed by these authors in each case represent errors in experimental reproducibility. Jeffery et al. (1966) report one standard deviation of 0.6 kbar, Haygarth et al. (1967) 0.5 kbar, and Zeto et al. (1969) 0.52 kbar.

A few comments are in order concerning systematic errors in these three studies. Jeffery, et al. (1966) and Haygarth, et al. (1967) were forced to use the midpoint of the transition in up and down pressure cycles. For Jeffery, et al. this involved only sample hysteresis of 2.6 kbar; for Haygarth, et al. it involved both apparatus and sample hysteresis totaling approximately 5.4 kbar, while Zeto, et al. performed an equilibrium experiment. If one takes the center of the region of indifference as the calibration point, uncertainties due to hysteresis are small in the work of Jeffery, et al. (1966), large in the work of Haygarth, et al. (1967), and non-existent in the work of Zeto, et al. (1969).

Jeffery's work involves error due to uncertainty in the theory of approximately two percent. Zeto's work involves a serious and unknown extrapolation error which could be of the order of 2 kbar. In view of these comments, the following are estimates of uncertainties for each measurement:

Jeffery, et al. (1966)	Reproducibility	0.6 kbar
	Theory	1.1 kbar
	Hysteresis	1.3 kbar
Haygarth, et al. (1967)	Reproducibility	0.5 kbar
	Hysteresis	2.7 kbar
	Corrections	0.2 kbar
Zeto, et al. (1969)	Reproducibility [5]	0.52 kbar
	Extrapolation	2.0 kbar

Since the uncertainties in the three cases are of approximately the same magnitude and are in large measure just estimates, it appears illogical to give greater weight to any one of these measurements in calculating a "best value".

The various reported values for the Ba I–II transition are given in table 7. The commonly available barium used for calibration is approximately 99.5 percent pure. The "best value" of 55.3 kbar is given for this material and represents the average of the values reported by the three groups mentioned. The other work is not felt to be of comparable validity. The value for the initiation of the transition on compression will vary in each piece of equipment and must be calibrated in terms of the equilibrium point. The error flag for the best value represents a judgment by the reviewers.

d. Bismuth III–V

As discussed above, the so-called "high Bi point" now known as the Bi III–V was reported in routine

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[5] This error involves uncertainties in the mercury and bismuth points and uncertainties in temperature.