was observed to increase through repeated cycling while that of iron decreased (Bassett, private communication).

c. Sample Purity

The substance should be obtainable with high and readily reproducible purity. It should also be chemically stable and relatively easy to handle. There is no general relation regarding the effect of sample impurities on a transition pressure. Transition pressures of some materials are relatively unaffected by impurities while others are relatively sensitive.

In work by Zeto, et al. (1968) on bismuth, the equilibrium transition pressure was essentially independent of purity (six 9's vs two 9's), microstructure (single-crystal vs extruded polycrystal), and thickness of the samples.

Gschneidner, et al. (1962) studied the cerium $\gamma-\alpha$ transformation pressure as a function of rare-earth impurity. The effect of lanthanum, praseodymium, dysprosium, and lutecium additions is to increase the $\gamma-\alpha$ transformation pressure. Lanthanum, the largest solute atom, raised the transformation pressure the most while lutecium, the smallest atom, raised it the least.

Brandt and Ginsburg (1963) studied the effects of antimony and lead impurities on the Bi I–II, II–III transition pressures. Lead atoms which are about the same size as bismuth atoms did not appreciably affect the nature of the phase diagram in concentrations up to 1.26 percent.

Antimony, however, at increased concentrations caused the width of Bi II to become more narrow until at solute concentration of 0.8 percent it disappeared. The Bi I–III phase transition then produced a volume change of 7.5 percent equal to the sum of the changes (4.5%, 2.9%) of the Bi I–II and Bi II–III transitions.

Bundy (1965) reports that the addition of cobalt or vanadium impurities to iron increases the Fe $\alpha-\epsilon$ transition pressure. The rate of increase was much greater with vanadium (whose size is larger than iron) than with cobalt (whose size is almost identical to iron).

Work by Darnell (1965) indicates that with alkali halides, anionic impurities have little effect on the transition pressure while the cationic seem to have a very marked effect. It is interesting to note that in all of the work cited above, the effects are negligible at impurity levels of less than 0.1 percent.

While chemical stability is of little problem with most calibrants, the oxidation problem encountered with cesium and barium can be minimized through more careful handling procedures.

d. Transformation Characteristics

The temperature dependence of the transition pressure dP/dT should be small. Where this is not possible, dP/dT should be known to good accuracy, which condition implies that temperature be measured to consistent accuracy.

The transition should take place at a sharply defined equilibrium pressure with a small region of indifference as defined in section 1. In the work of Bridgman (1940a), the region of indifference of the Bi I–II transition was 60–100 bar at 30 °C. Dadson and Greig (1965) found a point at which pressure changes of 0.1 bar in either direction reversed the mercury transition. This phenomenon illustrates the superiority of liquid-solid transitions. It has been common to select the midpoint of the region of indifference as the thermodynamic equilibrium point, which condition is not necessarily true. It can be seen that a wide region of indifference places a large uncertainty on the transition point.

The materials presently employed as pressure calibrants do not possess all the desirable characteristics discussed. In cases where a poor characteristic exists, it is of greater importance to understand the implication of the constraints imposed. As pointed out previously, the constraints of the pressure-transmitting medium must be better understood if conditions deviate from hydrostatic assumption.

3.2. Error Analysis

In high pressure work where calibration studies for a particular material seem to be giving a convergent trend toward some particular value, a 'best value' has been evaluated for the point. The 'best value' for the transition pressure of calibrants discussed in this review is determined on the basis of a weighted average of the significant published values. The weight used for a particular value is the square reciprocal of the standard deviation. This approach requires that each author make a complete analysis of all possible sources of systematic error associated with his work and estimate properly the accuracy. If an author has failed to do this, a best value which is unduly biased toward the work of this particular author results. In situations where this analysis has not been made, the error has been reevaluated by the reviewers in order to make an equitable comparison. We emphasize the fact that for calibration studies, past or future, a detailed evaluation of the possible sources of systematic error is as important as the determination of the measured value itself.

One of the difficulties in intercomparing various papers is the fact that authors often present insufficient data and descriptive detail for the reviewer to make an objective evaluation of errors. Furthermore, the uncertainties presented in some calibration papers are uncertainties in the reproducibility of the experimental point and do not represent a realistic evaluation of the absolute accuracy. In order to present worthwhile data, an author needs both to discuss and evaluate all possible sources of systematic error. If, in addition to experimental measurements, one makes use of some

theory, he must take into consideration the uncertainty introduced in the theory.

3.3. Fixed Points Below 30 Kbar

Early in his work Bridgman (1911a) recognized the value of using manganin wire resistance gages to measure hydrostatic pressure. Bridgman measured the effect of pressure on manganin wire and found that there was no appreciable temperature effect between 0 °C and room temperature. (In order for these gages to be reliable they must be annealed and then calibrated against a standard.) Bridgman's (1911b) first manganin gages were calibrated against the free-piston gage up to a pressure of 12 kbar. The sensitivity of the free-piston gage used was about 8 bar and that of the manganin gage about 2 bar. The results of this calibration demonstrated that the change of electrical resistance of manganin is nearly linear with pressure enabling it to be calibrated by a single pressure at some fixed point.

a. Mercury

The freezing point of mercury at 0 °C was selected for this calibration point. Pressures were measured with a manganin gage which had been previously calibrated against a free-piston gage. The data published at this time (1911) presented the value of 7620 kg/cm² (7.472 kbar)[4] for the liquid-solid transition pressure at 0 °C. In later years (1940) he states that this point "was measured in the first place with an absolute gage and taken in all my work to be 7640 kg/cm² (7.492 kbar)" (Bridgman, 1940b). According to Babb (1963) the final value (7640 kg/cm²) was the average of the six determinations; two detected by volume change and the other four by electrical resistance.

Bridgman's work on mercury, as reported in 1911, was never re-examined until the work of Johnson and Newhall in 1953. These investigators developed a controlled-clearance piston gage as opposed to the re-entrant type cylinder of Bridgman, as discussed in section 2. Pressures were determined with a gold chromium gage, a manganin resistance gage, and by the F/A (force/area) method. The transition pressure in this determination is 109, 760 ± 750 psi (7.568 kbar) compared to Bridgman's value of 7.492 kbar. In consequence of an unusually large experimental error of ± 0.7 percent, these two values are in fair agreement.

The next calibration study of Hg was made by Zhokhovskii (1955). He felt that though the fixed point of Hg at 0 °C was convenient due to its reproducibility, it was insufficient for calibration purposes. Consequently, he determined the melting curve of mercury up to 10 kbar. For this purpose the pressure cell is placed in a liquid bath to guarantee stable temperatures. The temperature of the interior of the cell was measured by a thermocouple which had sensitivity of 0.005 °C. For the determination at $t = 0$ °C, the bath was

filled with melting ice. The measurement of pressure was accomplished by the use of a manganin gage which had been previously calibrated against a free-piston gage. The method of detecting the phase boundary was based on changes of pressure and temperature at the transition.

The temperature at the ice point turned out to be 0.035 °C due to the flow of heat into the cell, while the pressure at this point was 7722 kg/cm² (7.573 kbar). For greatest accuracy this one measurement was made with the free-piston gage. The experimental data were then represented by the empirical Simon-type equation with three empirical constants:

$$\log (P + 37663) = 1.21458 \log T + 1.69765, \qquad (1)$$

where P is in kbar and T is in kelvins. From the slope of this smoothed curve he extrapolated the pressure from its value at $T = 0.035$ °C to 0 °C and obtained an equilibrium transition pressure for the mercury liquid-alpha transition of 7715 kg/cm² (7.566 kbar). No precise limits of error or evidence as to the dispersion of the data on which this result is based are given.

In later investigations Zhokhovskii, et al. extended the melting curve of mercury up to 20 kbar (1957) and to 25 kbar (1959a). In this work they have fitted 64 experimental points to equation (1) over the range up to 25 kbar, which corresponds at 0 °C to the smoothed value of 7719 kg/cm². Values of P/P_c were calculated for each of the experimental points. The majority of the deviations lie within ± 0.3 percent to ± 0.5 percent. In the region below 15 kbar the observed deviations ΔP_i tend to be mostly positive, while above this value they are distributed mostly on the negative side, which distribution indicates a systematic discrepancy.

In 1963, Newhall, Abbot, and Dunn, using an improved version of the controlled-clearance piston gage, arrived at the value of 7.5654 kbar for the mercury point at 0 °C. The temperature was at 0.002 °C; however, no details of temperature measurement are given. The value given is based on a single determination so no details are available as to the reproducibility of the data or the dispersion within a series of measurements.

In 1965, Dadson and Greig (1965) of the Standards Division of the National Physical Laboratory in England published the results of a very thorough and careful investigation on the freezing pressure of mercury. While most of the previous workers utilized the volume change of mercury to identify the transition point, these measurements employed the change of electrical resistance of the mercury sample. The magnitude of this change is of the order 4:1 at 0 °C. This method has the advantage of using very small quantities of mercury so that the effect of volume changes at the transition point is significantly minimized.

The constant temperature bath used was of the type employed for the calibration of precision thermometers

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[4] In this section the actual numbers and units reported by the original sources are given to indicate the intended number of significant figures. The value transferred to kbar units will be shown in parentheses.