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A Redetermination of the Freezing Pressure of Mercury Using Improved Apparatus and Technique

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A number of improvements in apparatus and technique have been made since the production of the prototype model of the controlled-clearance piston gauge used by Johnson and Newhall in their 1953 determination of the freezing pressure of mercury at 0°C. These improvements and the importance of this value have justified the redetermination reported herein.

The nature and scope of modern high and ultra-high pressure research have indicated that known fixed points on the pressure scale need careful reestablishment. Most of these fixed points were determined by Dr. P. W. Bridgman, whose primary urge was broadly to survey the whole field of high pressure, leaving detailed scrutiny to those who might follow him. He expressed regret that little had been done to corroborate his values. In recent years, however, many experimenters have found it important to repeat and extend his work, particularly in the higher ranges. In 1911 Bridgman located the melting curve of mercury and thereafter used the equilibrium pressure at 0°C as a fixed point in the calibration of his manganin-wire resistance gauges, just as the ice point and the boiling point of water at normal atmospheric pressure are used for the calibration of thermometers. His value of 7640 kg/cm² was obtained by means of a free-piston gauge, and was supposed to be accurate to about 1/2 of 1 per cent. In 1953 Johnson and Newhall described the controlled-clearance piston gauge, or dead-weight tester, which provides a substantial gain in accuracy over the reentrant type developed by Bridgman. In their paper they reported a determination of the mer-
cury 0° C. freezing pressure, stating the value 109,760 plus or minus 750 psi. Continued improvement in the quality of the Harwood piston gauges and the availability of somewhat better pressure fluids have suggested the opportunism of a redetermination of this fixed point.

**APPARATUS**

In essence the experiment consists of placing a sample of mercury in a bomb which is then immersed in a constant-temperature (ice) bath and subjected to increasing pressure until the mercury is observed, by some convenient means, to freeze, and in measuring this pressure by means of a free-piston gauge which is connected to the bomb.

The bomb containing the mercury was the cell body of a conventional Harwood manganin gauge, having a cavity of 1 in. diam by about 5 in. long, with a pressure port at the lower end, and at the upper end a closure containing a single electrical lead and a ground terminal.

As recommended by Bridgman, the freezing point was first observed with a sample contained in a fixture illustrated in Figure 1. Its resistance, about ½ ohm, decreased on freezing by a factor of about 3, readily observable with a Leeds and Northrup Wheatstone bridge, Type S. Results were unsatisfactory, and rather than attempt the indicated modifications it was decided to make use of the volume change, about 3 per cent. For this purpose a sample, about ½ cu in. in volume, was placed in the stainless-steel container shown in Figure 2. The threaded closure was channeled so as to provide free access of the pressure fluid, but to act as a baffle preventing loss of mercury in the event of a sudden and violent leak.

The controlled-clearance piston gauge in this experiment is a Harwood DWT 1000 with a piston nominally 0.01 sq in., intended to support a load of 1000 lb. (There was no harm in applying a 10 per cent overload to attain the required pressure, while there would have been a distinct loss in accuracy in using the next smaller piston.) For several reasons this is definitely superior to the piston gauge, the prototype DWT, used by Johnson and Newhall. The greatest advantage lies in the increase of the piston cross-sectional area by a factor of 4. The modern DWT's are provided with better thrust and guide bearings and have better geometry in critical parts of the piston and jacket cylinder. There has been a substantial improvement in manufacturing techniques, resulting in pistons and cylinders of much higher quality. The piston finally used was examined at the Van Keuren Company and its diameter was reported as between 0.112835 and 0.112840 in., whereas the nominal diameter is 0.112838 in.; in measurements at ½2-in. intervals no deviation as large as 0.000005 in. was observed. In contrast, there was a distinct taper in Johnson and Newhall's piston. The jacket cylinder disclosed no flaw under observation with a 50-power microscope. In addition to the physical improvements in the DWT we now make a more precise evaluation of the effective area of the piston.

Associated with the DWT 1000 is a panel-mounted system in which
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Fig. 1.—Resistance sampleholder.

A—Polyethylene block
B—Polyethylene tubing, 0.034 in. i.d., 3/16 in. o.d., 8 in. long
C—Mercury
D—Polyethylene base
E—Mica washer
F—Electrodes

Fig. 2.—Sample holder for change of volume.
are incorporated two intensifiers—one supplying the measured pressure of the piston, the other for the jacket pressure controlling the clearance around the piston. For precision the latter pressure was measured by means of a manganin resistance gauge and Carey-Foster type bridge.

The bath of melting ice was contained in a plastic tub of about 18 in. diam by 21 in. deep, distinctly larger than that used by Johnson and Newhall. The tub was wrapped in a large polyethylene sheet and set in a wooden box of 20 x 20 x 26 in. which was in turn placed within a wooden box of 31 x 31 x 32 in. The intervening spaces were filled with vermiculite. The interior of the tub was meticulously cleaned, and the manufactured ice was rinsed before use. A motor-driven stirrer provided active circulation. The quality of insulation is indicated by the fact that some ice remained in the bath 160 hours after the last charging.

Fifty-two inches of 8H austenitic stainless tubing, ½ in. o.d. by 3/32 in. i.d., led from the pressure port at the lower end of the mercury cell to the nearest cross and the rest of the pressure system, the first 27 in. submerged in the ice bath. This compares with 3 or 4 in. of submerged tubing in the Johnson and Newhall experiment.

Pure white Amoco gasoline was used in the mercury cell and in the associated pressure system as far as the valve, \( V_1 \), shown in Figure 3. The DWT 1000, on the other hand, was supplied with a mixture of equal parts Univis P-38 and Isopar H, both products of Esso Standard and Humble Oil and Refining Company. These choices were made in the interest of fluidity and low viscosity within the ice bath, combined with good lubrication of the rotating piston in the DWT 1000. Procedure was such as to prevent more than a very slight mingling of the liquids.

The mercury cell was independently subjected to pressure by means of a priming pump (Blackhawk), \( I \), and intensifier, \( F \). The free space at the low-pressure end of the intensifier was filled with colored liquid which was piped to a sight glass, \( J \), to show the displacement of the intensifier piston and the change in volume of the mercury and gasoline.

Two Harwood Carey-Foster type bridges were used in the experiment. One was applied to a manganin cell, \( E \), for precise knowledge of the jacket pressure, \( P_j \), exerted in the DWT 1000. The other, with the manganin cell, \( C \), connected directly to the mercury cell, made it possible to read the pressure on the mercury at any time.

A special comparison bridge, including two matched 120-ohm manganin coils joined by a shunted potentiometer slide wire, was connected to the manganin cells \( C \) and \( D \). Its function was to indicate equality of pressures on either side of the valve \( V_1 \), that the DWT 1000 might be applied to the mercury cell with no more disturbance of the system than that caused by changing the volume within that valve when it was opened.

The experiment was performed in a constant-temperature room wherein the thermometer readings ranged from about 21.5 to 23.0° C. This afforded relative freedom from undesirable currents and other disturbances.
A re-determination of the freezing pressure of mercury

**Fig. 3.**—Arrangement of apparatus.

A—Mercury cell  
B—Free-piston gauge, DWT 1000  
C—Manganin cell, for measuring mercury pressure, \( P_{Hs} \)  
C′—Manganin cell, for comparing mercury pressure  
D—Manganin cell, for comparing piston pressure, \( P_m \)  
E—Manganin cell, for measuring jacket pressure, \( P_j \)  
F—Intensifier for mercury cell  
G—Intensifier for measured pressure  
H—Intensifier for jacket pressure  
I—Blackhawk hand pumps  
J—Sight glass  
\( V_1, V_2, \ldots, V_s \), valves

**PROCEDURE**

With the valve, \( V_1 \), closed, gasoline was pumped into the mercury cell, building up pressure, until freezing began, as indicated in the first setup by a sudden decrease in resistance and in the second by the drop in pressure corresponding to the loss in volume of the mercury. Pumping was continued until roughly one-half the mercury was frozen, when the system was allowed to reach equilibrium. A little gasoline was now released, with a momentary reduction of pressure, which permitted a little mercury to melt, and its increasing volume automatically re-established pressure equilibrium. The piston gauge was loaded as nearly
HIGH-PRESSURE MEASUREMENT

as possible to equal pressure as shown by the comparison bridge; the valve, $V_1$, was opened, and the weights were adjusted to final balance (Figure 4).

Recognition of final balance was achieved on the basis of a preliminary experiment with the DWT-1000. Its piston is free to travel in a vertical range of about 1/8 in. With the valve, $V_1$, closed and with a given load (known to be approximately that which would subsequently be required to balance the freezing pressure of the mercury), enough Univis-Isopar mixture was pumped in to lift the piston to the top of its range. For a series of jacket pressures, including the particular value applied for the final balance, the rate of fall of the piston was observed as the liquid mixture leaked out through the crevice between the piston and the jacket cylinder. It can be shown that for a fixed load, that is, for fixed pressure, $P_m$, supporting the piston, there is a linear relation between the jacket pressure, $P_j$, and the reciprocal of the cube root of the fall rate:

$$P_j = R + S (F)^{-1/3}$$

(1)

where $F$ is the time of fall and $R$ and $S$ are constants. This relation was used later in the calculation of the clearance between the piston and the cylinder. For the immediate purpose, the fall rate with the actual jacket pressure was the criterion of equilibrium when the final balance was being made. This will be understood from the following consideration: With the valve, $V_1$, closed and the DWT piston at the top of its travel a specific volume of liquid is defined in the space under the piston and in the piping as far as the valves, $V_1$, and $V_2$. Some of this leaks out through the crevice between piston and cylinder at a definite rate depending on the piston pressure, $P_m$, and on the clearance, controlled by the jacket pressure, $P_j$; and the piston falls at a definite rate to take up the lost volume. Suppose that the valve, $V_1$, is opened. If the pressure in the mercury cell is not stable and equal to the piston pressure, liquid may flow from the DWT toward the mercury cell, freezing more mercury as the pressure there is increased, and allowing the piston to fall at an increased rate; or the opposite may occur. The final balance was accordingly made by adding or subtracting a few grams to the load on the piston until the fall rate was the same as before the valve, $V_1$, was opened. This technique turned out to be surprisingly sensitive; the load balance could be determined to about one gram in 500,000 grams.

Since one of the corrections to be applied in the determination of the cross-sectional area of the piston involves the temperature of the carboloy piston a very rough experiment was performed wherein the large end of the secondary piston (the steel extension of the carboloy piston) was immersed in a bath of warm water and the gradient to the tip of the carboloy was measured.

The pressure, $P_m$, measured by the piston gauge is, by definition, $W/A_E$, where $W$ is the total force applied by the piston and $A_E$ is the effective area of the piston. $W$ includes the weight of the piston, the supporting hanger for the weights, and a compensating weight to make
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Fig. 4.—Record of pressure, change of volume experiment.

A—Freezing begins
B—Pumped gasoline
C—Pumped gasoline
D—Pumped gasoline
E—Released gasoline
F—Connected DWT 1000

a "tare" of precisely 20 lb, as well as the main load of nearly 1100 lb. These weights are all traceable to the National Bureau of Standards and are accurate to better than 0.001 per cent. The effective area is taken as the arithmetic means of the area of the piston and the bore of the jacket cylinder:

\[ A_e = \frac{A_p + A_\varepsilon}{2}. \] (2)

The area of the piston as determined by the Van Keuren Co. was subject to corrections for the distortions under load, as indicated with great exaggeration in Figure 5. If \( A_\sigma \) is the area as measured and \( A_p \) the area under experimental conditions we have

\[ A_p = A_\sigma \left[ 1 + \left( \frac{\Delta A}{A_\sigma} \right)_{r_m} + \left( \frac{\Delta A}{A_\sigma} \right)_{\tau} \right] \] (3)

where the \( \Delta \)'s represent the effect of loading and of temperature, respectively. The effect of loading may be determined by the theory of elasticity:

\[ \left( \frac{\Delta A}{A_\sigma} \right)_{r_m} = -(1 - 3\mu) \frac{P_m}{B_c} \] (4)
where $\mu$ is Poisson's ratio and $E_c$ is Young's modulus for carboloy. The effect of temperature is

$$
\left( \frac{\Delta A}{A_o} \right)_T = 2\alpha_c(T - T_o)
$$

(5)

where $\alpha_c$ is the linear coefficient of expansion of the carboloy, $T$ is the temperature of the piston in use and $T_o$ the temperature at which $A_o$ was measured.

In the final determination the cross-sectional area of the bore of the jacket cylinder was calculated by a new method. Referring to Figure 6, the intercept on the vertical axis gives the jacket pressure required for infinite time of fall, which means no leak, the bore of the cylinder exactly fitting the piston. If $\Delta P_j$ is the difference between the intercept and the actual jacket pressure, by applying the principle of superpositions we have

$$
A_c = A_p \left[ 1 + \left( \frac{\Delta A}{A_o} \right)_{P_j} \right]
$$

(6)

where $A_c$ is the area of the bore of the cylinder at operating conditions and from the theory of elasticity we may write

$$
A_c = A_p \left[ 1 + \frac{4w^2}{E_s(w^2 - 1)} \Delta P_j \right]
$$

(7)

where $w$ is the ratio of the inner to the outer radius of the cylinder and $E_s$ is Young's modulus for the steel of which the cylinder is made.
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![Graph](image)

Fig. 6.—Relation of rate of fall, \( T \), to jacket pressure \( P_j \).

Ordinates: Jacket pressure, psi/1000

Abscissa: \[ \frac{1}{\sqrt{T \text{ime to fall 0.050 in., sec}}} \]

Double circle indicates operating point

RESULTS

No final result was computed for the resistance experiment.

The results obtained with the first attempt at observing change of volume, using a substandard piston, agree with our final results within the stated accuracy, but for avoidance of confusion will not be reported here.

For the final determination the following values were used or observed:

- Total floating weight \( \ldots \) 1098.03 lb (±0.01)
- Measured cross-section of piston \( \ldots \) 0.0100000 in.\(^2\) (±0.0000005)
- Actual jacket pressure \( \ldots \) 80,220 psi (±100)
- Jacket pressure to fit \( \ldots \) 88,200 psi (±400)
- Temperature of measurement of piston \( \ldots \) 20° C. (±1° C.)
- Estimated running temperature \( \ldots \) 40° C. + 10° C. — 5° C.
- Young's modulus, carboloy, \( E_c \) \( \ldots \) 90 \( \times \) 10^6 psi (±0.5 \( \times \) 10^6)
- Poisson's ratio, carboloy \( \ldots \) 0.22 (±0.005)
- Temperature coefficient of expansion, carboloy \( \ldots \) 4.42 \( \times \) 10^-6 (±0.01)
- Young's modulus, steel \( \ldots \) 30.0 \( \times \) 10^6 psi (±0.5)
- Poisson's ratio, steel \( \ldots \) 0.28 (±0.005)
- Wall ratio, jacket cylinder \( \ldots \) 6.9 (±1.0)
- Time of fall, 0.050 in., DWT isolated \( \ldots \) 17.9 min
- Time of fall, DWT on Hg cell \( \ldots \) 18.2 min
- Change in time of fall for 10 grams unbalance \( \ldots \) —0.6 min
- Adjusted total floating weight \( \ldots \) 1098.04 lb (±0.01)
- Correction for gravity, Pendulum Station
- No. 788 \( \ldots \) —35.4 psi

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Correction for buoyancy, stainless-steel weights ........................................... -16.5 psi
Correction for 50 in. head of oil ................................ 1.5 psi
Correction for ice bath at 0.002° C .................................. -6 psi
Correction for conduction of heat along pressure tubing, 6, 12 .......... negligible
Adjustment to absolute pressure ................................... 14.8 psi

From these values, with the corrections specified above, we obtain the final result of 109,729 psi which is equivalent to 7565.4 bars (or, for comparison with Bridgman's 7640, to 7714.9 kg/cm²).

The last five corrections are all minor and in their sum they introduce an uncertainty of less than 10 psi. More serious is the situation with respect to the effective area, as will appear in the following table, listing all the possible errors to be considered to be of importance:

TABLE I
PERCENTAGE OF ERROR

<table>
<thead>
<tr>
<th>Description</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective area, measurement of diameter</td>
<td>±0.001</td>
</tr>
<tr>
<td>Effective area, temperature uncertainty</td>
<td>±0.004</td>
</tr>
<tr>
<td>Effective area, elastic constants, carboloy</td>
<td>+0.005, -0.010</td>
</tr>
<tr>
<td>Effective area, elastic constants, steel</td>
<td>±0.017</td>
</tr>
<tr>
<td>Five corrections</td>
<td>±0.008</td>
</tr>
<tr>
<td>The resultant uncertainty is estimated to be</td>
<td>+0.045 or -0.05</td>
</tr>
</tbody>
</table>

DISCUSSION AND CONCLUSIONS

It was disappointing that the attack via resistance change was unsuccessful. With precautions to assure free melting and freezing, with no possibility for superposed stress in the sample, the method is unquestionably more convenient. Examination of Bridgman's data confirms this view.

The sluggishness of the freezing and melting of the volume sample was much greater than had been anticipated. Two considerations appear to account for most of this. First, although the pressure-transmitting liquid was chosen largely because of its low viscosity, the length of tubing was appreciable. Nevertheless, the time delay in pressure transmission should not be noticeable, and the pressure increase due to temperature rise incident to viscous flow in the pipes must be very slight. It is worth noting that in a recent test a mixture of 10 parts white gasoline with 1 part Univis P-38 transmitted 200,000 psi from one manganin cell to another through a 10-ft tube, ¼ in. i.d., immersed in a trough of melting ice with no delay observable by ordinary means.

More important is the heating effect due to compression or decompression as liquid is pumped in or released. The mercury cell contains space for more pressure fluid than is desirable. This is the consequence of adapting available apparatus elements. One of us recalls the setup in
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Professor Bridgman's laboratory for checking manganin gauges against mercury, where the mass of mercury and bomb were comparable but the length of tubing was much less and the volume of transmitting fluid probably less than one-half of our amount, and the pressure responses were much more rapid.

The principal virtues of the present experiment lie in the unusually favorable condition and operation of the free-piston gauge, in the very satisfactory arrangement of the mercury cell and ice bath, providing a high degree of constancy in temperature and complete freedom from pressure leak, and in the procedure whereby, after approximate adjustment by means of the manganin gauges and the bridges, the free-piston gauge was applied directly to the mercury pressure.

The present experiment serves to emphasize an important consideration in the use of deadweight testers. The technique of equalizing fall rates gave very gratifying confidence in the precision of our pressure reading. This depended, however, on the absence of leaks in the system, for it would be very difficult to distinguish between the fast fall due to a pin-hole in a tube connection and a similar effect as pressure fluid flowed toward the mercury to compensate for loss of volume on freezing.

It was not surprising to find after three days not the slightest detectable pressure change in the mercury cell (which had been left untouched in the ice bath), and to observe only a slight pressure increase, attributable to a slight rise in temperature at the bottom of the bath after ten days.

ACKNOWLEDGMENT

It is a pleasure to acknowledge our indebtedness to Prof. F. Birch for valued consultation, to Mr. R. E. Wallace for technical assistance, to the staffs of the Engineering Metrology and the Pressure Vacuum Sections, National Bureau of Standards, and to Mr. K. Emery and to Mr. R. Lamport of the Van Keuren Company for piston measurement, and to Dr. R. W. Hickman for making available a supply of pure mercury.

REFERENCES


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DISCUSSION

D. P. Johnson (National Bureau of Standards, Washington, D. C.): For pressures greater than those reached by Bourdon and other elastic pressure gauges, and up to the highest reached with liquid pressure media, the manganin wire pressure gauge has been particularly successful. Many experimenters have followed the lead of P. W. Bridgman and calibrated the manganin gauge at the freezing pressure of mercury, usually at 0°C. For this reason during the past half century much of the experimental work at high pressures has been related to Bridgman’s value of 7640 kg/cm² or 7492 bars, based on his work of 1909–1912.

The first published redetermination of this value was that of Johnson and Newhall in 1954. This was followed by that of Zhokhovskii in 1955. Recent measurements by Dadson and Grieg have not been published, but their provisional value was reported to this symposium by Babb. Newhall, Abbott and Dunn are reporting a determination to this symposium. A report on a determination by Cross, Hill and Cooke is in preparation. These results are summarized in Table A. For purposes of comparison, all values are converted to bars.

Bridgman published no estimate of systematic errors in the value he adopted. The determinations reported in his 1912 paper fell in the range from 7590 to 7730 kg/cm². The subsequent determinations are included in this range. Johnson and Newhall estimated their accuracy at ±750 psi, about 50 bars. The four latest determinations appear to have accuracies within 2–5 bars.

TABLE A
FREEZING PRESSURE OF MERCURY AT 0°C.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>psi</th>
<th>kg/cm²</th>
<th>Bars</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>Bridgman</td>
<td>7640</td>
<td>7492</td>
<td></td>
</tr>
<tr>
<td>1954</td>
<td>Johnson &amp; Newhall</td>
<td>109760</td>
<td>—</td>
<td>7568</td>
</tr>
<tr>
<td>1955</td>
<td>Zhokhovskii</td>
<td>7715</td>
<td>7565.8</td>
<td></td>
</tr>
<tr>
<td>1962</td>
<td>Newhall, Abbott &amp; Dunn</td>
<td>109739</td>
<td>7715.4</td>
<td>7566.2</td>
</tr>
<tr>
<td>1962</td>
<td>Dadson &amp; Grieg (provisional)</td>
<td>7723</td>
<td>7573.7</td>
<td></td>
</tr>
<tr>
<td>1962</td>
<td>Cross, Hill &amp; Cooke (provisional)</td>
<td>—</td>
<td>7565</td>
<td></td>
</tr>
</tbody>
</table>

While some further improvement in accuracy may be expected, there should be no substantial change from the values obtained in the last decade.

The recent determinations of the mercury point are about 1 per cent higher than that of Bridgman. This is in line with the difference between Bridgman’s value for the Ice I–Ice II water triple point, 2115 kg/cm², and the provisional 2093 bars or 2133 kg/cm² by Johnson, Cross, and Cooke and reported by Lloyd and Johnson⁵.

Babb has pointed out other cases in which the agreement between Bridgman and others would be improved by a slight upward adjustment of the Bridgman scale.

Alfred Bobrowsky (Pressure Technology Corporation of America, Woodbridge, New Jersey): As long as there is liquid leakage past the piston, there will be a shear force built up on the piston itself. This shear stress is proportional to the rate of shear, and even though the liquid velocity is low, the clearance is small, and the rate of shear could be quite high. I wonder if there is any correction that could be made for the additional force on the piston due to the liquid shear stress?

Stephen Groves (Harvard University, Cambridge, Massachusetts): I have questions on two matters: The first concerns the convenient method of measuring the freezing point of mercury by measuring a discontinuity in the resistance. I gather from what you have said that your difficulties were due to mercury contamination. Assuming proper care, would you agree with Johnson that this is a perfectly good method? Are there changes in design that you would recommend for your resistance-determination capsule?

The second question concerns the uncertainty associated with Bridgman’s value. We see 0.1 per cent quoted. Is this correct, and if so, where was his error underestimated?

D. M. Warschauer (Raytheon Company, Waltham, Massachusetts): I have found in past resistance determinations, although not made to

the accuracy you are talking about, that the purity of the mercury was important and that the electrodes had a lot to do with how pure the mercury remained during the experiment. How pure was your mercury and how did you make your electrodes?

E. W. Comings (University of Delaware, Newark, Delaware): The experiments are evidently very precise and the results the most accurate presently available. The authors are to be commended—especially on perfecting the equipment described. Answers to some further questions would be of interest:

1. How was the rate of fall of the piston observed?
2. The procedure described for relating rate of fall to jacket pressure is for a constant piston gauge pressure, \( P_m \). This is, no doubt, the equilibrium melting pressure. For use at other pressures, what is the function of \( P_m \) which permits this relation to be used?
3. Please restate the feature of the experiments which provided "complete freedom from pressure leak".
4. Is it feasible to state some of the general principles applicable to the design of the apparatus which precluded the use of the resistance—or which would lead to a suitable design? The article mentions features of Professor Bridgman's apparatus but leaves the reader to infer the significance to design.

AUTHORS' CLOSURE

Reply to Bobrowsky: The point raised by Dr. Bobrowsky has been covered in detail; among other places, in the paper by Bennett and Vodar, "Calibration of a Controlled-Clearance Pressure Balance up to 8,000 Bars", presented at this symposium, and by Meyers, and Jessup, our reference no. 11, pp. 1070, 1083.

Reply to Groves: With respect to Dr. Groves' first question, we should normally prefer the change-of-resistance method for observing the freezing point, since the effect is of very much greater magnitude than the change of volume. Our difficulty apparently arose from the fact that in cleaning the capillary containing the sample of mercury we missed some foreign matter discovered after the run. In repeating the experiment we would use a larger capillary. It is highly important to arrange the sample so that no parasitic stresses occur with freezing. One must assure that the ends of the sample, in freezing, do not act as a plug obstructing transmission of pressure toward the middle, creating a gradient between the measured ambient pressure and a somewhat lower pressure inside the capillary. This would have the result of making the apparent freezing pressure somewhat higher than the true value.

Regarding his second question, we refer to the above discussion by Dr. Johnson. It will be noted that the value of 7714.9 kg./cm.\(^2\) falls within the range reported in 1912 by Bridgman, though near the upper end. One of us (R. H. Abbot), whose association with Bridgman began in 1930, recalls his statement of accuracy, "about \( \frac{1}{10} \) per cent", but can only guess as to the cause of the discrepancy.
Reply to Warschauer: We agree that it is most important to use mercury of the highest purity. Otherwise the sharpness of the freezing or melting transition is lost. Our mercury was obtained by exchange with the Lyman Laboratory of Harvard University, due to the courtesy of the director, Dr. R. W. Hickman. It has been purified chemically and by distillation.

Our electrodes were made from low-carbon steel, supposed to be inert with respect to mercury, particularly when subject to hydrostatic compression.

(1) Reply to Comings: The rate of fall was measured by attaching an Ames dial gauge, reading to 0.0001", to the top of the piston and observing the time of piston fall by means of a stop watch. The force of the dial stem was added to the weights hung on the piston.

(2) This question can best, perhaps, be answered by reviewing the general procedure for use of a controlled-clearance, dead-weight tester.

A small load, say ¼ of the nominal total weights, is placed on the piston and enough pressure, $P_m$, (approximately 25 per cent of range) is applied to float it. Jacket pressure, $P_j$, is built up until the leak has been reduced enough to make the fall time measurable with significant accuracy. With the same $P_m$ a series of fall times are measured with increasing jacket pressure (until the limit of time available is reached). The results are plotted as in Figure 6 and the best straight line drawn. $P_m$ is now increased to about ½ the nominal weight, $P_m$ 50 per cent, and a second series of fall times observed. Similar sets of readings are taken for $P_m$ 75 per cent, and $P_m$ 100 per cent. The results appear as shown in the full lines of Figure 7(a). A second plot is now made, Figure 7b, the jacket pressure, $P_j$, intercepts against the corresponding $P_m$'s. It will be noted that for any of the $P_m$'s the $P_j$ intercept is the jacket pressure required to make the fall time infinite, which means there is

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Fig. 7.—(a) Second series of observed fall times. (b) Second plot of jacket pressure.
no leak, the crevice being completely closed, or, in other words, the bore of the cylinder exactly fitting the piston. For this condition the piston is effectively seized, or stalled, being unable either to rise or to fall or to rotate. For this reason the curve of Figure 7(b), which turns out to be a straight line, has been called the "stall curve". The $P_j$ intercept of the "stall curve" may be checked by very cautiously applying jacket pressure, with no pressure under the piston, until seizure is noted when the piston is rotated by hand. In using a dead-weight tester a fall time is selected which will provide sufficient opportunity to make the necessary adjustments and readings for the particular experiment. For this fall time and the applicable $P_m$, the $P_j$ is read from Figure 7(a) and plotted against the $P_m$ on Figure 7(b). Two points obtained in this manner will determine a line, shown with dot-dash in Figure 7(b), which indicates a desirable relation between $P_m$ and $P_j$ for any use of the dead-weight tester. It is worth noting that at long fall times the quality of the dead-weight tester and pressure system is disclosed. If there is a minute leak in the system the piston falls faster, compensating for the extra loss in fluid, and destroying the linearity of the graphs of Figure 7(a). This will displace the observed points to the right, causing the line to curve upward as it approaches the jacket pressure axis. Such an effect will also appear if either the piston or cylinder is slightly out of round, or if either is scored longitudinally. When the points lie close to the straight line an excellent instrument is indicated.

For high values of measured pressure, the operator should be mindful of the possibility of structural change in the pressure fluid, which would affect its viscosity. This would show up as a change in the slope of the "stall curve".

(3) "Complete freedom from leak" was due to effective design and good workmanship in the connections and fittings, double-cone and Bridgman types, and in the valves $V_1$, $V_4$ and $V_5$, Figure 3. The wording in our text was somewhat loose at this point.

(4) Principles relating to the design of apparatus for observing change of resistance on freezing have been discussed in the reply to Dr. Groves. Re-stated briefly, one should assure that the freezing or melting of the mercury is unattended by the creation of any stress in the sample, and that all material involved is inert to mercury.