

The Construction, Operation and Performance of a Primary Standard Mercury Column for the Measurement of High Pressures

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THE CONSTRUCTION, OPERATION AND PERFORMANCE OF A PRIMARY STANDARD MERCURY COLUMN FOR THE MEASUREMENT OF HIGH PRESSURES

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The most satisfactory primary pressure gauge for measuring low pressures is the open mercury column, but, for pressures above about 30b, the practical difficulties caused by the great height of such a column preclude its use (1 bar, abbreviated b = 10^6 dyn/cm²). In order to calibrate free-piston gauges at higher pressures, a column of 'reduced height' has been designed and constructed which will measure static pressures up to 2500b with an accuracy of $\pm 0.15b$ at the maximum pressure.

This consists of a mercury-in-steel column about 900 cm tall, connected to steel end-blocks at both extremities. Two oil lines containing liquid paraffin are used to transmit pressure to the top and the bottom of the column, the position of the mercury-oil interfaces being located by electrical contacts fixed in the end-blocks. The vertical distance between the two mercury menisci is obtained

from the distance between the exposed ends of the insulated plugs which obturate the contacts. This height is measured to ± 0.013 cm by a calibrated Invar tape, with the aid of suitable levels for making a horizontal transfer from each reference point to the tape. The mercury column and the oil line connected to the upper end-block are enclosed in a well-lagged jacket, through which water is circulated from a thermostatically controlled tank maintained at 25°C . The mean temperature of the column which is known to $\pm 0.02^{\circ}\text{C}$ is estimated from the temperature of the water, measured by mercury-in-glass thermometers as it enters and leaves the jacket. A high-pressure valve manifold connected to the two oil lines enables the pressure at the top or the bottom of the column to be transmitted to one or other of two sensitive free-piston gauges.

In operation, the pipe line connected to the top of the column is first opened to atmospheric pressure, and a free piston gauge is connected to the foot of the column. The pressure balanced by this gauge, which may be calculated from the hydrostatics of the system, is then reproduced at the top of the column by oil pressure, with the same free-piston gauge now connected to the top oil line. The second free-piston gauge is then connected to the foot of the column, and the pressure at which it is balanced is equivalent to the pressure at the foot during the first operation, plus the pressure due to the mercury column itself. By repeated interchanges of the two free-piston gauges, the pressure is increased to 2500b in increments of pressure equivalent to the pressure drop across the column, which is about 11.5b.

The accurate calculation of the pressure drop across the column, as a function of pressure, requires a knowledge of the compressibility of mercury and of the liquid paraffin. The results for the compressibility of mercury obtained previously by both static and dynamic measurements are compared, and it is shown that there are large discrepancies between the results obtained by various authors. Possible sources of error in the experimental methods are briefly discussed, and by correlating the most reliable results an equation is developed which expresses the compression of mercury at 25°C as a function of pressure up to 3000b. Measurements of the compressibility of liquid paraffin with a re-entrant type Pyrex glass piezometer are described and values of the compression are tabulated at 15, 20 and 25°C , and pressures up to 2500b. The compression of pure benzene was also measured at 25 and 40°C , and pressures up to 1000b, using the same apparatus, in order to ensure that there were no large systematic errors in the method. The average difference between these values and those obtained by previous workers is about 0.7%. Since benzene readily absorbs moisture from the air, it was distilled into the piezometers under vacuum using an apparatus which is briefly described.

Detailed consideration is given to the random experimental errors and to possible systematic errors in the measurement of the pressure drop across the column, and in the determination of an absolute pressure using the primary pressure gauge. It is shown that the standard deviation of the pressure drop, $1.1 \times 10^{-3}\text{b}$ at 2000b, arises principally from the uncertainty in the compressibility of liquid paraffin and mercury. On the other hand, the accuracy of the absolute pressure measurements depends in part on the error in the measurement of the pressure drop, but chiefly on the accuracy with which the pressures can be transferred from the bottom to the top of the column. The transfer error arises from uncertainty as to the temperature of the piston and the sensitivity of the free-piston gauges. With the gauges described, it is shown that the standard deviation of the pressure measurement at 500b should be about $\pm 0.015\text{b}$ (one part in 34000), and at 2500b $\pm 0.14\text{b}$ (one part in 18000).

1. INTRODUCTION

High pressures are commonly measured by gauges which make use of a variety of secondary effects, such as the elastic deformation of a metal tube, the compressibility of a liquid, or the change of electrical resistance of a wire. These gauges have to be calibrated initially, and at frequent intervals of time, against a primary pressure gauge which may take the form of a mercury column or a balanced free-piston gauge. Since a large number of free-piston gauges are in use, the accuracy and sensitivity of which are dependent largely upon constructional features, it is desirable that their constants should be checked from time

to time against a few master gauges, which in turn have been compared with a standard of international status. It is with the construction, operation and accuracy of such a standard gauge that this paper is concerned.

2. THE DISADVANTAGES OF THE FREE-PISTON GAUGE AS A PRIMARY GAUGE

The operation of the simplest form of free-piston gauge may be understood by reference to figure 1. The pressure, P , to be measured is transmitted by means of some suitable liquid to the underside of a cylindrical steel piston, A , which fits closely in a steel block, B . The piston is free to move, but is restrained by counterbalancing weights supported on its upper end.

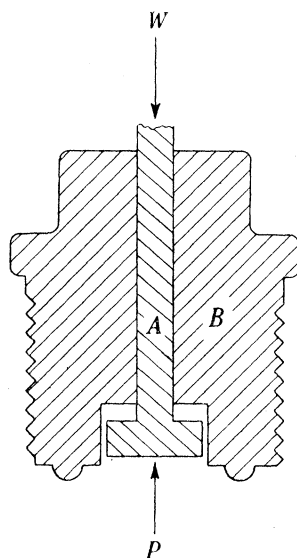


FIGURE 1. Diagram of a piston and cylinder assembly for a free-piston gauge.

If p is the atmosphere pressure, W the total load of the counterbalancing weights, w the 'effective weight' of the piston and A its cross-sectional area, all measured in self-consistent units, then, under ideal conditions, when the piston is in equilibrium,

$$P = \frac{(W+w)}{A} g + p. \quad (2.1)$$

The main assumptions implied in this relationship are that the piston is truly cylindrical and free to move in the cylinder without friction, that there is no measurable leak of liquid past it, and that no distortion of the piston or cylinder takes place under pressure.

In practice, none of these assumptions is strictly valid. In particular, the leakage of liquid past the piston is a function of pressure and results in a lifting force on the piston owing to viscous drag, which is equivalent to an increase in the effective area of the piston. If the dimensions of the piston and the cylinder remain unchanged under the stresses arising from the working pressure, it can be shown that the effective area may be taken, without serious error, to be the mean of the cross-sectional areas of the piston and the cylinder. Attempts have been made to calculate the effective area by direct measurement of the diameter of both the piston and the cylinder, but, since the piston may have a nominal area of less than 0.02 in.², it is difficult to make such measurements accurately.

An alternative procedure is to measure the diameter of the piston as accurately as possible, and then to estimate the width of the gap between the piston and cylinder from measurements of the rate of leakage past the piston or the torque required to rotate it. The effective area calculated from these results, however, seldom agrees with that obtained by comparing the gauge with a mercury column even at low pressures.

The assumption that the piston and cylinder undergo no elastic deformation is inadmissible at high pressures and the effective area must be considered to be a function of the pressure.

$$\text{Thus } P = \frac{(W+w)}{(A_e)_P} g + p, \quad (2.2)$$

where $(A_e)_P$, the effective area at pressure P , is a function of the pressure.

Bridgman (1911*a*) has used the theory of elasticity to estimate the effect of distortion on the effective area of a piston; he calculated that, for his particular gauge, the effect would require a correction of about one part in 500 at 10000b (1 bar, abbreviated b, is equivalent to 10^6 dyn/cm²). A similar calculation by Michels (1924) indicated that, at 200b, the increase in the effective area of his differential piston would be one part in 11500, but he could not detect such a change, since his observations were only accurate to one part in 3000. Later, Keyes & Dewey (1927) showed that, of two gauges tested, one indicated the true pressure up to 160b, the pressure limit for which it was designed, whereas the other indicated slightly higher pressures than the true value above about 400b. The discrepancy increased to one part in 11000 at about 600b. For work of the highest accuracy, therefore, the free-piston gauge cannot be considered as a primary gauge, and it is necessary to calibrate it by comparison with a pressure standard of another type.

3. DESIGN, LAY-OUT AND OPERATION OF THE STANDARD GAUGE

The 'standard gauge' to be described is a modification of the column gauge of reduced height originally developed by Holborn & Schultze (1915) at the Physikalisch-Technische Reichsanstalt and later modified by Keyes & Dewey (1927). It consists of a mercury-in-steel column some 30 ft. high, to each end of which is connected a free-piston gauge. These two gauges are used alternately to record increments of pressure each equal to the pressure exerted by the mercury column. By repeated interchange of the gauges connected to the top and bottom of the column, in a manner to be described later, pressure measurements may be made up to the limit of 2500b, for which the column, gauges and accessory fittings are designed.

(a) *Lay-out of the column*

The lay-out of the column and ancillary equipment is shown diagrammatically in figure 2, plate 4. The column consists of an inverted U-tube, one limb, M , of which is filled with mercury, and the other, N , with liquid paraffin. The mercury limb consists of a 30 ft. long stainless-steel pipe, connected at each end to a stainless-steel block, F , into which electrical contacts held in insulated plugs, E , are screwed. These contacts, together with an electronic relay and two indicator bulbs, serve to locate the position of the mercury-oil interfaces. The column is connected to the remainder of the apparatus by stainless-steel pipe-lines, D and C , containing liquid paraffin, connexion being made

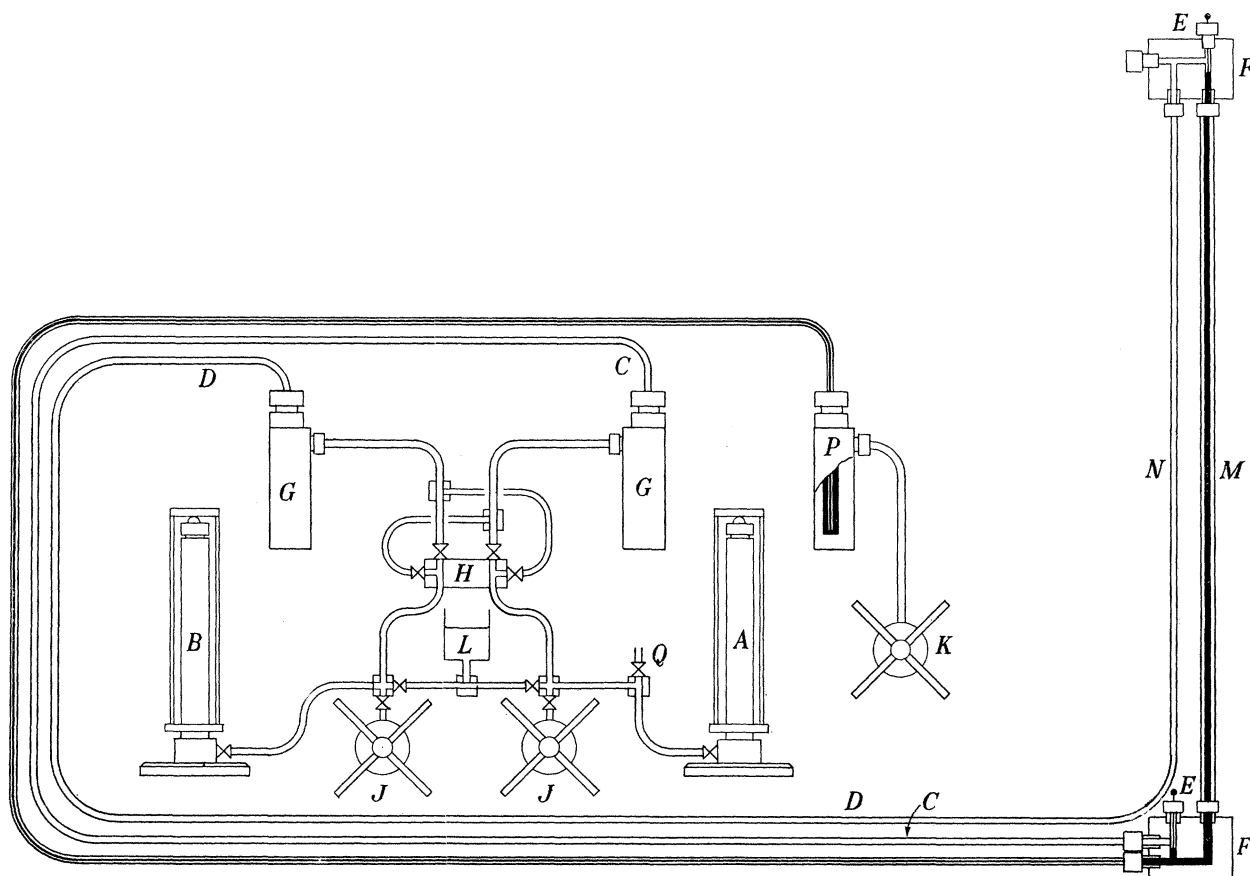


FIGURE 2. The lay-out of the mercury column and the ancillary high pressure equipment shown in diagrammatic form.

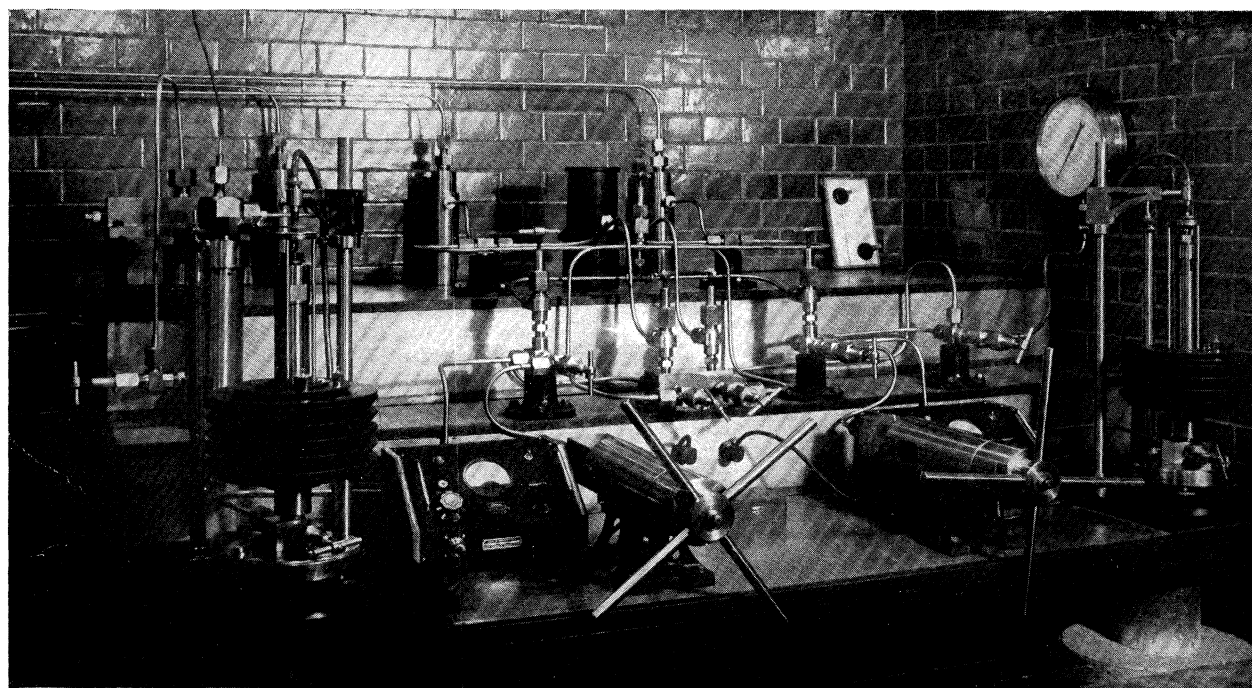


FIGURE 3. Photograph of the working bench.

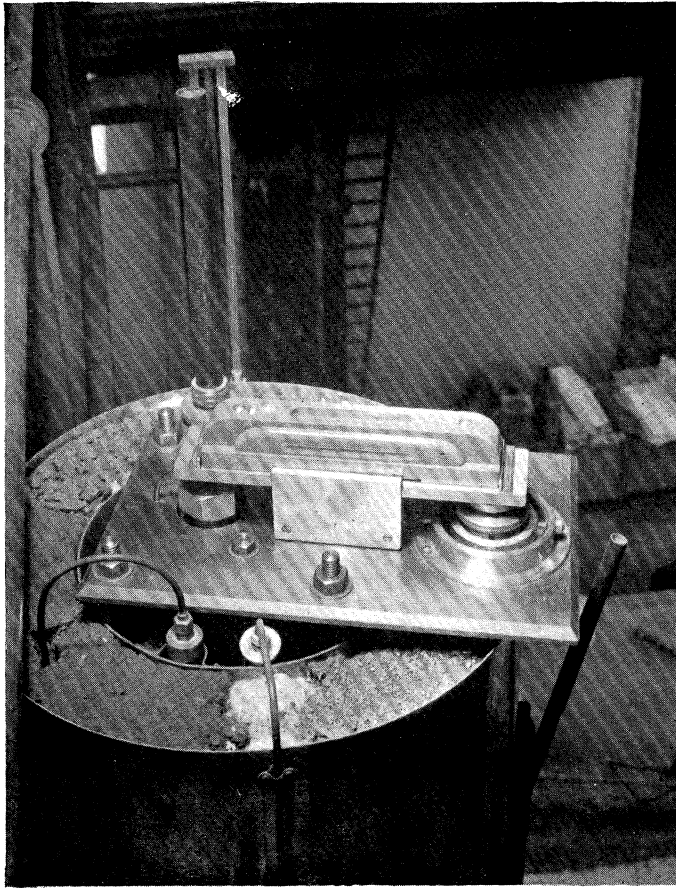


FIGURE 4. Photograph of the top of the mercury column.

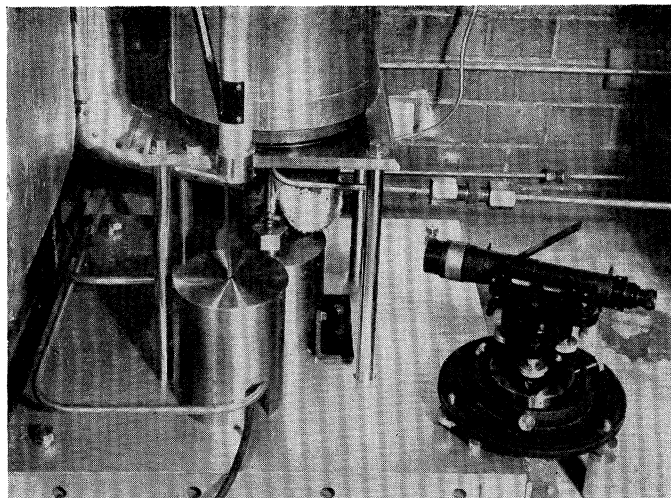


FIGURE 6. Photograph of the base of the mercury column with the lagging removed.

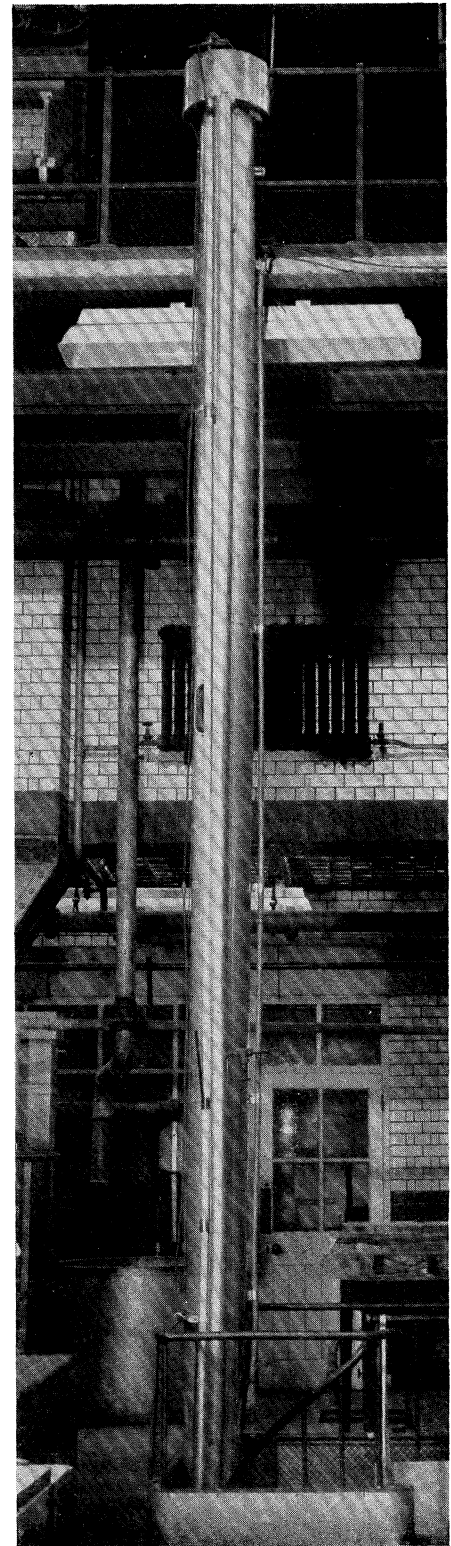


FIGURE 5. Photograph of the mercury column.

through the two end-blocks. Both the mercury column, M , and the return line, N , are enclosed in a cork-lagged jacket (not shown in the figure), through which water is circulated from a thermostatically controlled tank. The length of the mercury column is measured by an Invar tape which is suspended from the top of the column. A high-pressure valve manifold, H , connected to the two oil lines, enables the pressure at the top or the bottom of the column to be transmitted to one or other of two free-piston gauges, A and B . Each gauge is provided with a screw ram injector, J , by means of which the pressure applied to the top or the bottom of the mercury column may be varied. Provision is made to connect an oil reservoir, L , to either injector, so that the latter, after being isolated from the system by closing the appropriate valves, may be primed at atmospheric pressure. The oil bottles, G , act as traps to prevent any mercury from the column reaching the remainder of the apparatus and, also, by increasing the volume of the system, serve as pressure accumulators, thus diminishing the effect of the small but inevitable oil leak past the pistons in the free-piston gauges. As the pressure in the column increases, the volume of the mercury decreases owing to its compressibility and the internal volume of the steel column increases owing to the elastic expansion of the tube. Thus, it is necessary to add mercury to the foot of the column, by means of the small injector, K , and the mercury trap, P , until contact is made with both electrodes. The three-way block, Q , is included in the system to provide means for connecting the standard gauge to some other piece of apparatus should it be required. The arrangement of the various components on the working bench is shown in the photograph (figure 3, plate 4) and the column is shown in the photograph (figure 5, plate 5).

(b) *Pressure closures*

The pipe-line containing the mercury is made up of three 10 ft. sections of tubing which are connected by flanges; the joints being made by self-tightening lens rings. The various pressure vessels are closed by screwed plugs provided with metal to metal conical seats. The pipe-line connexions are made by turning hemispherical seatings on the ends of the pipe and coupling the pipes to manifolds by means of collars and nuts. No welded or soldered joints and no gaskets are used.

Detailed designs of the various forms of closures are given by Newitt (1940).

(c) *Materials of construction*

For the construction of all parts of the system subject to moderate stresses, an austenitic nickel-chromium alloy steel, in the fully annealed condition, has been employed. This alloy steel (British Standard Specification 970-En. 58) has been found to resist satisfactorily mercury action, by penetration and amalgamation, up to pressures of 5000 b. For exceptionally highly stressed items of equipment, a high tensile nickel-chromium-molybdenum steel (British Standard Specification 970-En. 25) has been used.

The maximum shear-stress theory of elastic failure (Newitt 1940) has been used to calculate the minimum wall thickness of all the items of equipment, a factor of safety of two based upon the yield stress being employed. The connecting pipes consist of solid drawn austenitic capillary tubing, cut to length, with suitable seatings machined on the ends.

The liquid used to transmit the pressure from the two ends of the column to the free-piston gauges has to have the property of retaining fluidity at room temperature, at the highest working pressure. In addition, it must have an electrical conductivity small enough to preserve the electrode potential. Liquid paraffin B.P. has been found suitable for this purpose.

(d) *Situation of the standard gauge*

The mercury column has been erected in the Hydraulics Laboratory of the Imperial College of Science and Technology, South Kensington. The foot of the column, the free-piston gauges and the ancillary equipment are housed in a small well-insulated room below floor level. The column rises through the laboratory and is anchored to steel girders supporting a gallery, which gives access to the top of the column.

(e) *Operation of the gauge*

Several methods are available for using the pressure standard to calibrate a free-piston gauge. One method is as follows.

With reference to figure 7, the top of the mercury column is first opened to atmospheric pressure by connecting the oil pipe-line, D , to the oil reservoir, L , while the base is connected to the free-piston gauge, A . By adjusting the load on the gauge and the various injectors, equilibrium is attained so that the mercury just makes contact at the top and bottom electrodes, while the piston of the gauge is in a floating position. Since the pressure difference between the top and the bottom of the column can be accurately calculated from a consideration of the hydrostatics of the system, a knowledge of the atmospheric pressure enables the pressure at the gauge A to be calculated. If, now this pressure is accurately reproduced at the top of the column by gauge A , while gauge B is connected to the base, then at equilibrium, when both pistons are floating and the mercury column is of requisite length, the pressure at the bottom may be calculated. Repeated pressure transfers enable the pressure at the bottom of the column to be increased until the limit for the apparatus is attained. By comparing the load on the gauge connected to the bottom of the column with the calculated pressure for each operation, the effective area of the gauge may be calculated as a function of pressure.

The pressure at the base of the column at the end of the first operation, P_1 , is given by

$$P_1 = p + \Delta P_1, \quad (3.1)$$

where p is the atmospheric pressure, and ΔP_1 is the pressure drop across the column for the first operation.

If the pressure P_1 is transferred without error to the top of the column, then the pressure at the base of the column at the end of the second operation, P_2 , is given by

$$P_2 = P_1 + \Delta P_2, \quad (3.2)$$

where ΔP_2 is the pressure drop across the column for the second operation. Thus

$$P_2 = p + \Delta P_1 + \Delta P_2. \quad (3.3)$$

In general, the pressure at the base of the column after the N th operation is given by

$$P_N = p + \sum_1^N \Delta P. \quad (3.4)$$

This procedure is very laborious, since about 175 pressure transfers are necessary to obtain a pressure of 2000 b. A simpler calibration may be made in the following manner. A free-piston gauge is balanced against some unknown but accurately reproducible pressure and the load on the piston observed. The unknown pressure is then applied to the top of the mercury column and the gauge balanced against the pressure at the bottom by increasing the load on the piston. If it is assumed that the effective area of the piston does not change over a pressure range equivalent to the difference in pressure between the top and the bottom of the mercury column, the effective area of the piston may be calculated from the increase in the load on the piston and the known pressure drop across the column.

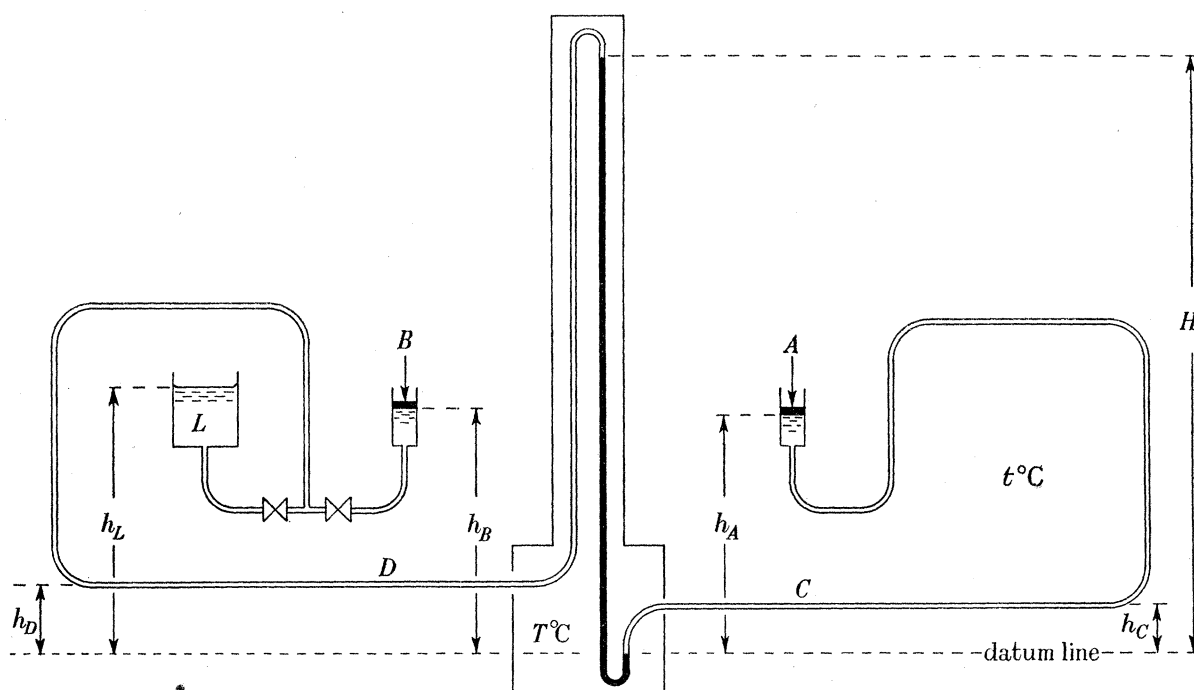


FIGURE 7. Diagram showing the hydrostatic heads of mercury and liquid paraffin which have to be considered when calculating the pressure drop across the column.

When the free-piston gauge is balanced against a reproducible pressure P ,

$$P = \frac{W_1 g}{(A_e)_1} + p_1. \quad (3.5)$$

If the pressure, P , is now connected to the top of the column and the gauge to the base, then at equilibrium

$$P + \Delta P = \frac{W_2 g}{(A_e)_2} + p_2, \quad (3.6)$$

where p is the atmospheric pressure,

W_1 and W_2 are the total loads on the free-piston gauge,

$(A_e)_1$ is the effective area of the piston gauge at pressure P , and

$(A_e)_2$ that at pressure $P + \Delta P$.

If $(A_e)_2 = (A_e)_1$, then

$$(A_e)_1 = \frac{(W_2 - W_1) g}{\Delta P + p_1 - p_2}. \quad (3.7)$$

If the experiment is repeated at a higher pressure, any change in the effective area of the piston with pressure may be calculated. In practice, the reproducible pressure may conveniently take the form of another free-piston gauge.

4. CALCULATION OF THE PRESSURE DIFFERENCE ACROSS THE COLUMN

In figure 7, the various hydrostatic heads which form part of the total pressure measured by the column are shown. If the gauge B is connected to the top of the mercury column and if the gauge A is connected to the bottom of the column, then, assuming that the acceleration due to gravity is independent of height, that the apparatus is free from air and that all the pipe-lines and equipment outside the water jacket are at the same temperature as the ambient air in the laboratory, it can be shown that at equilibrium:

- if P_A = pressure acting on the face of the piston in gauge A ,
 P_B = pressure acting on the face of the piston in gauge B ,
 P_M = pressure at the mid-point of the mercury column, M ,
 ΔP = pressure difference between the top and bottom of the column,
 g = acceleration due to gravity at Imperial College,
 H = height of the mercury column above datum line passing through lower mercury-oil interface,
 h_A = effective height of the piston in gauge A above datum,
 h_B = effective height of the piston in gauge B above datum,
 h_C = height of the oil pipe line, C , above datum,
 h_D = height of the oil return line, D , above datum,
 h_L = height of the oil surface in reservoir, L , above datum,
 ρ = density of mercury,
 σ = density of liquid paraffin,
 T = mean temperature of mercury column, and
 t = mean temperature of ambient air in the laboratory,

then

$$\Delta P = P_B - P_A = g[H\rho^T - h_C\sigma^T - (h_A - h_C)\sigma^t - (H - h_D)\sigma^T + (h_B - h_D)\sigma^t]. \quad (4.1)$$

The density in each of the above terms is evaluated at the mean pressure of the column of liquid to which the term refers. Since the rate of change of density with pressure is small, the pressure at the mid-point of columns $(H - h_D)$ and $(h_B - h_D)$ may be taken as P_B and $(h_A - h_C)$ as P_A , while that at the mid-point of column H is P_M .

If equation (4.1) is rewritten with subscripts to represent the pressure at which the density is evaluated and superscripts for the temperature, then, on rearrangement of the terms, we obtain

$$\Delta P = g[H(\rho_{P_M} - \sigma_{P_B})^T + h_C(\sigma^t - \sigma^T)_{P_A} - h_D(\sigma^t - \sigma^T)_{P_B} - h_A\sigma_{P_A}^t + h_B\sigma_{P_B}^t]. \quad (4.2)$$

Since $P_B - P_A$ is only about 11.5 b,

$$(\sigma^t - \sigma^T)_{P_A} \simeq (\sigma^t - \sigma^T)_{P_B}.$$

Writing

$$h_e = h_B - h_A, \quad (4.3)$$

then
$$\Delta P = g[H(\rho_{P_M} - \sigma_{P_B})^T + h_e\sigma_{P_A}^t - h_B(\sigma_{P_A} - \sigma_{P_B})^t + (h_C - h_D)(\sigma^t - \sigma^T)_{P_M}]. \quad (4.4)$$

Since $(\sigma_{P_A} - \sigma_{P_B})^t$ and $(\sigma^t - \sigma^T)_{P_M}$ are both small quantities, the contribution towards the pressure difference, ΔP , made by the last two terms in equation (4.4), is less than 20 dyn/cm, i.e. one part in 500 000. Thus

$$\Delta P = g[H(\rho_{P_M} - \sigma_{P_B})^T + h_e \sigma_{P_A}^t]. \quad (4.5)$$

5. CALCULATION OF THE ERROR IN THE PRESSURE MEASUREMENT

It is convenient to discuss the error in the measurement of a pressure, P , in two parts: first the error in the measurement of the pressure differences across the column, and then the error in the pressure transfers from the bottom to the top of the column.

It is well known that, if $X = f(x_1, x_2, \dots, x_n)$, where f is any function, then

$$V(X) = \left(\frac{\partial X}{\partial x_1}\right)^2 V(x_1) + \left(\frac{\partial X}{\partial x_2}\right)^2 V(x_2) + \dots + \left(\frac{\partial X}{\partial x_n}\right)^2 V(x_n), \quad (5.1)$$

provided that x_1, x_2 , etc., vary independently, where $V(X), V(x_1)$, etc., are the variances of X, x_1 , etc. Thus

$$S(X) = \sqrt{\left[\left(\frac{\partial X}{\partial x_1}\right)^2 S(x_1)^2 + \left(\frac{\partial X}{\partial x_2}\right)^2 S(x_2)^2 + \dots + \left(\frac{\partial X}{\partial x_n}\right)^2 S(x_n)^2\right]}, \quad (5.2)$$

where $S(X)$ is the standard deviation of X and $S(x_1), S(x_2), S(x_n)$, etc., are the standard deviations of x_1, x_2, x_n , etc.

In many cases the standard deviation of an independent variable is not known and an estimate cannot be based on observational scatter. Consider the variable x_n , where x_n is a function of the directly measured quantities y_1, y_2 , etc. Although standard deviations cannot be assigned to y_1, y_2 , etc., estimates based on experience may be made and values may be ascribed within which the maximum error is known to lie. If $\Delta y_1, \Delta y_2$, etc., are these limits for the measured quantities, y_1, y_2 , etc., then the maximum error of $x_n, \Delta x_n$, is derived from the following differential formula:

$$\Delta x_n = \frac{\partial x_n}{\partial y_1} \Delta y_1 + \frac{\partial x_n}{\partial y_2} \Delta y_2 + \dots + \frac{\partial x_n}{\partial y_m} \Delta y_m. \quad (5.3)$$

Algebraic signs are arbitrarily assigned to each of the individual errors, so that they will all act to increase the value of Δx_n . In the absence of further information, we shall assume the value of Δx_n to represent $3S(x_n)$ of an error which is normally distributed. Thus, $\frac{1}{3}\Delta x_n$ may now be treated as a standard deviation and the value substituted in equation (5.2). In cases where we have reason to suspect that the distribution is not normal, the value Δx_n is assumed to be the standard deviation of the independent variable x_n ; this results in a conservative estimate of $S(X)$.

Occasionally, the results of the error analysis are translated into a statement of proportional accuracy; unless otherwise stated, it is the standard deviation which is thus expressed as a proportion.

Although care has been taken to ensure that all the known errors are as small as possible and that they are completely random, a fiducial assessment of the absolute accuracy of the standard gauge is only possible by comparing it with a number of different precision primary gauges.

6. ERROR IN THE MEASUREMENT OF THE PRESSURE DIFFERENCE ACROSS THE COLUMN

It has been shown that $\Delta P = g[H(\rho_{P_M} - \sigma_{P_B})^T + h_e \sigma^t]$.

$$\text{Thus } S(\Delta P) = \sqrt{\left[\left(\frac{\partial \Delta P}{\partial \rho^T} \right)^2 S(\rho^T)^2 + \left(\frac{\partial \Delta P}{\partial \sigma^T} \right)^2 S(\sigma^T)^2 + \left(\frac{\partial \Delta P}{\partial H} \right)^2 S(H)^2 + \dots \right]}. \quad (6.1)$$

Detailed consideration will now be given to each of the independent variables in turn and an estimate of their standard deviation will be made.

(a) *Density of mercury*

It can be shown that the density of mercury at some pressure, P , and temperature, T , is given by

$$\rho_P^T = \frac{\rho_0^0}{(1 - \bar{\beta}^T P)(1 + \bar{\alpha} T)}, \quad (6.2)$$

where ρ = the density of mercury, the superscript denoting the temperature and the subscript the pressure, subscript zero signifies atmospheric pressure,

$\bar{\alpha} = \frac{1}{V_0^T} \left(\frac{\Delta V}{T} \right)_0$ per °C is the mean coefficient of thermal dilation at atmospheric pressure,

and $\bar{\beta} = \frac{1}{V_0^T} \left(\frac{\Delta V}{P} \right)^T$ per b is the mean coefficient of isothermal compressibility of mercury at T° C and pressure P bars.

$$\text{Thus } \rho_P^T = \frac{\rho_0^0}{(1 - k_P^T)(1 + \bar{\alpha} T)}, \quad (6.3)$$

where $k_P^T = (V_0^T - V_P^T)/V_0^T$ is the isothermal compression at T° C and pressure P bars.

Thus, the error in the density of mercury at any pressure P and temperature T arises from a combination of the errors involved in the measurement of the base density of mercury at 0° C and atmospheric pressure, the compression of mercury, the mean coefficient of thermal dilation of mercury and the mean temperature of the mercury column.

Hence, from equation (6.3),

$$S(\rho_P^T) = \sqrt{[K^2 S(\rho_0^0)^2 + L^2 S(k_P^T)^2 + M^2 S(\bar{\alpha})^2 + N^2 S(T)^2]}, \quad (6.4)$$

where

$$\begin{aligned} K &= 1/(1 - k_P^T)(1 + \bar{\alpha} T), \\ L &= \rho_0^0/(1 - k_P^T)^2(1 + \bar{\alpha} T), \\ M &= -\rho_0^0 T/(1 - k_P^T)(1 + \bar{\alpha} T)^2, \\ N &= -\rho_0^0 \bar{\alpha}/(1 - k_P^T)(1 + \bar{\alpha} T)^2. \end{aligned}$$

In the following subsections, we examine the published results for the base density, the coefficient of dilation and the compression of mercury to obtain the most reliable values for these variables and an estimate of their standard deviation.

(i) *Base density at 0° C and atmospheric pressure*

The usual method of purifying mercury, by distillation under reduced pressure, results in a partial separation of the isotopes; for this reason, the densities of different specimens vary slightly according to their past history. The most reliable values obtained for the density of mercury at 0° C and atmospheric pressure are given in table 1. The unweighted

mean of all these results is $13.59508_6 \text{ g/cm}^3$, and the standard deviation of the mean is $\pm 0.00005_7 \text{ g/cm}^3$. Birge (1941) gives the value of the density of mercury as $13.59504_0 \pm 0.00005_7 \text{ g/cm}^3$ but it is difficult to agree with him that the investigations prior to 1925 should be rejected. Until the results of a new determination of the density of mercury, now being made by the National Physical Laboratory, are published, we shall assume that the internationally recognized value for the base density of mercury, 13.59510 g/cm^3 , is correct and ascribe to it a standard deviation of $\pm 0.00006 \text{ g/cm}^3$.

TABLE 1. BASE DENSITY OF MERCURY AT 0°C AND ATMOSPHERIC PRESSURE

author	base density (g/cm^3)
Marek (1883), adjusted by Scheel & Blankenstein (1925)	13.59506
Thiesen & Scheel (1898)	13.59507
Guye & Batuecas (1923)	13.59509
Scheel & Blankenstein (1925)	13.59511
Batuecas & Casado (1936)	13.59501
Batuecas & Fernández Alonso (1948)	13.59518
unweighted mean	13.59508 ₆
standard deviation of mean	$\pm 0.00005_7$

(ii) *Thermal dilation*

Beattie, Blaisdell, Kaye, Gerry & Johnson (1941) have made some very accurate measurements of the thermal dilation of mercury over the temperature range 0 to 350°C , which they represented by the equation

$$\frac{V - V_0}{V_0} \times 10^8 = \bar{\alpha}t \times 10^8 = 18144.01t + 70.16 \times 10^{-2}t^2 + 28.625 \times 10^{-4}t^3 + 2.617 \times 10^{-6}t^4, \quad (6.5)$$

where t is the temperature $^\circ \text{C}$ int. scale.

In table 2 are given the mean coefficients of thermal dilation over the temperature range 0 to 100°C , calculated from this and other recent dilation equations.

TABLE 2. VALUES OF THE MEAN COEFFICIENTS OF THERMAL DILATION OF MERCURY ACCORDING TO VARIOUS AUTHORS

temperature ($^\circ \text{C}$)	$10^8 \bar{\alpha}$, mean coefficient of thermal dilation ($^\circ \text{C}$)				
	James (1914)	Sears (Harlow 1914 <i>b</i>)	Harlow (1914 <i>a</i>)	Harlow (1929)	Beattie <i>et al.</i> (1941)
0	—	18146	—	18154	18144
25	—	18169	—	18174	18163
50	—	18194	18188	18192	18187
75	—	18221	18213	18216	18214
100	18241	18251	18244	18247	18245

Sear's (Harlow 1914*b*) equation is based on the results obtained by Chappuis (1907), Callendar & Moss (1912) and Harlow (1914*a*). The agreement of Beattie's coefficients with those of Harlow (1914*a*) is very good; the standard deviation estimated from nine observations over the temperature range 0 to 300°C being $2.0 \times 10^{-8}/^\circ \text{C}$. Later, Harlow (1929) recalculated his results, using new values for the mean coefficients of thermal dilation of silica obtained from a critical survey of all the available data. Beattie's coefficients are not in such good agreement with the new values, the standard deviation, estimated as before, being $7.7 \times 10^{-8}/^\circ \text{C}$.

Sears has pointed out that the values of the mean coefficients obtained by Callendar & Moss (1912) must be regarded as being affected by some unexplained source of error. This also applies to the values obtained at the Physikalisch-Technische Reichsanstalt from 1895 to 1919, and by Chappuis (1917); consequently, in estimating the absolute accuracy of Beattie's coefficients, we have rejected the earlier work.

The standard deviation of the mean dilation coefficient of mercury, given by the various authors in table 2, from those calculated using Beattie's formula is $4.6 \times 10^{-8}/^{\circ}\text{C}$, over the temperature range 0 to 100°C .

(iii) *Compression*

It is not easy to make a comparison of all the compression data which have been published for mercury, because of the differences in temperature and pressure ranges covered and the use of different pressure units.

If the results from static P - V - T measurements, which are usually presented in the form of mean compressibility coefficients over a given pressure range, are converted into compressions, an equation of the form

$$k_p^T = \left(\frac{V_0 - V_P}{V_0} \right)^T = aP - bP^2 - cP^3 - \dots, \quad (6.6)$$

may be fitted to the data, where a , b , c , etc., are temperature-dependent constants.

In the majority of cases, a quadratic equation is adequate to represent the compression data to within the experimental error of the original measurements. Thus

$$\beta^T = \frac{1}{V_0} \left(\frac{dV}{dP} \right)^T = a - 2bP, \quad (6.7)$$

where β^T is the true coefficient of compressibility.

Hence, the initial coefficient of compressibility at atmospheric pressure, $\beta_0^T = a$, and the rate of change of the coefficient of compressibility with pressure $(d\beta/dP)^T = -2b$.

In table 3, values of β_0 at 20°C , $d\beta/dP$ at approximately 25°C , and $\Delta\beta_0/\Delta T$, calculated from the work of the various authors, are given. Some of the work was done at one temperature only, not 20°C ; in these cases, the initial coefficients at 20°C , marked with an asterisk, were calculated using the average value of $(\Delta\beta_0/\Delta T) = 62.8 \times 10^{-10}/b^{\circ}\text{C}$. In all other cases, the measurements were either made at 20°C , or the mean temperature coefficient of compressibility obtained from the work of the author under consideration was used to calculate the initial coefficient of compressibility at 20°C .

The early work on the compression of mercury, carried out by Colladon & Sturm (1827), Aimé (1843), Regnault (1847), Grassi (1851), Amaury & Descamps (1869) and Tait (1888), has not been considered. It was done before the theory of elasticity was properly understood, and incorrect calculations of the change in volume of the piezometer were made frequently.

Amagat (1889*a*) measured the mean compressibility coefficient of mercury in glass piezometers over a pressure range not exceeding 0 to 50 atm at 15°C . The mean compressibility coefficients of the glasses used were measured by direct (Amagat 1889*b*) and indirect (Amagat 1888) methods. The former method gave results which were about

2.5% larger than the latter. If the true coefficient of compressibility of glass is taken as the mean of that obtained by both methods, the mean coefficient of compressibility of mercury at 15°C is $3.90 \times 10^{-6}/b$.

TABLE 3. COMPARISON OF THE COMPRESSIBILITY DATA FOR MERCURY
ACCORDING TO VARIOUS AUTORS

author	$10^6 \beta_0^{20}$ (/b)	$10^{10}(d\beta/dP)$ (/b ²)	$10^{10}(\Delta\beta_0/\Delta T)$ (/b ⁵ °C)
Amagat (1889 <i>a</i>)	3.93*	—	—
De Metz (1892)	3.86	—	87.3
Carnazzi (1903)	3.84	1.96	45.0
Richards & Stull (1903)	3.89	3.88	—
Richards & Brink (1907)	(3.88)	—	—
Bridgman (1909)	3.82	0.41	—
Bridgman (1911 <i>b</i>)	4.01	1.25	70.0
Dolezalek & Speidel (1920)	4.07*	1.81	—
Smith & Keyes (1934)	3.75	3.90	60.1
Hubbard & Loomis (1928)	4.01	—	48.3
Kleppa (1949)	3.94	—	66.0
unweighted mean	3.91	2.20	62.8
standard deviation	± 0.10	± 1.4	± 15.4

The mean compressibility coefficients at 0 and 19.4°C, over a pressure range of approximately 0 to 10 atm, were measured by De Metz (1892). The value of $\Delta\beta/\Delta T$ given in table 3 is applicable over the temperature range 0 to 20°C. Both Amagat and De Metz measured the compressibility coefficients of mercury over one pressure range only; thus it is not possible to calculate the initial coefficients at atmospheric pressure from their results. However, since the measurements were made at comparatively low pressures, their coefficients may be taken as those at atmospheric pressure without appreciable error.

Carnazzi (1903) measured the compressions of mercury at various temperatures between 20 and 200°C, at pressures up to 3000 atm, with a glass piezometer using glass compressibilities taken from Amagat's (1889*b*) work. The value of $d\beta/dP$ given in table 3 refers to 22.8°C and that of $\Delta\beta_0/\Delta T$ was calculated over the temperature range 20 to 200°C.

The differences between the mean compressibilities of mercury and glass at 20°C were measured by Richards & Stull (1903). Using Amagat's (1889*a*) value for the compressibility of mercury, and his observation that the compressibility of glass is approximately constant over the pressure range 0 to 1000 Kg/cm² (Amagat 1889*b*), they calculated the mean compressibility of mercury over various pressure ranges up to 600 Kg/cm².

Richards & Brink (1907) measured the difference between the coefficients of compressibility of iron and mercury and copper and mercury over the pressure range 100 to 500 atm at 20°C. Although the compressibilities of iron and copper were determined by direct measurements, that of iron was about 35% smaller than the more reliable value obtained by Bridgman (1935, 1940). If Bridgman's value is assumed to be correct, the mean coefficient for mercury from 100 to 500 atm is increased from 3.66 to $3.88 \times 10^{-6}/b$. Since there is no way of calculating the initial coefficient from Richards & Brink's measurement, their value is given in parentheses in table 3, and has been excluded from the calculation of the average initial coefficient at 20°C.

Bridgman (1909) measured the compression of mercury at 20°C and pressures up to 6500 Kg/cm², using a piston displacement piezometer made of iron, and obtained a value of $3.77 \times 10^{-6}/b$, for the initial coefficient. Later, Bridgman discovered an error in the calculation of the compressibility of iron, which when corrected increased the initial coefficient to $3.82 \times 10^{-6}/b$. It was suspected that the method gave values which were between 2 and 3% too low, consequently Bridgman (1911 *b*) redetermined the compression of mercury at 0 and 22°C, with a re-entrant type of iron piezometer over the pressure range 0 to 12000 Kg/cm². The value of $d\beta/dP$ given in table 3 is at 22°C and that of $\Delta\beta_0/\Delta T$ was calculated over the temperature range 0 to 22°C.

Measurements of the coefficients of compressibility at 24.6°C, over the pressure range 0 to 650 Kg/cm², were made by Dolezalek & Speidel (1920), using a method similar to that employed by Richards & Stull. It is not clear from the paper how the compressibility of the glass used to make the piezometer was obtained.

Smith & Keyes (1934) measured the compressibility of mercury from 30 to 300°C at pressures up to 350 atm. They employed a nickel piezometer and calculated the compressibility of nickel from the elastic constants. Above 200°C, the mercury amalgamated with the piezometer; consequently the value of $\Delta\beta_0/\Delta T$ was estimated over the temperature range 30 to 200°C only. The value of $d\beta/dP$ in table 3 is at 30°C. Unlike Carnazzi, who found the values of this derivative to be independent of temperature, these authors observed an increase with temperature.

Hubbard & Loomis (1928) and Kleppa (1949) measured the velocity of sound in mercury at atmospheric pressure, the former at temperatures from 0 to 70°C and the latter at 50 and 150°C. The values of $\Delta\beta_0/\Delta T$, which are given in table 3 and which are applicable over the temperature ranges 0 to 70°C and 50 to 150°C respectively, have been calculated from the isothermal compressibility coefficients obtained from the velocity of sound data.

If the mean values of the initial coefficient of compressibility and the rate of change of the coefficient of compressibility with pressure are combined, we obtain the equation

$$k_P^{20} = (3.90 \pm 0.1) P \times 10^{-6} - (4.4 \pm 2.8) P^2 \times 10^{-10}, \quad (6.8)$$

where P is the pressure in bars gauge. Thus

$$S(k_P^{20}) = P \times 10^{-6} \sqrt{(0.01 + 7.84P^2 \times 10^{-8})}. \quad (6.9)$$

At 1000b, $S(k_P^{20}) = 3.0 \times 10^{-4}$, which corresponds to an error of $\pm 8.5\%$ of the compression at that pressure.

This is a very large error, and it serves to show how difficult it is to obtain accurate values for the compression of mercury. The uncertainty arises chiefly because mercury has such a small compressibility that the correction for the change in volume of the piezometer, which may be 60% of the total volume change, is difficult to assess. Part of the error, however, may be attributed to impurities in some of the samples of mercury.

Although direct methods for measuring the compressibility of glass (Amagat 1889 *b*) gave more consistent results than indirect methods (Amagat 1888; De Metz 1892), the assumption that the piezometers had the same coefficient of compressibility as the test piece is doubtful, since the internal strains in glass are so difficult to remove. This is particularly true of those piezometers which have electrical contacts sealed into them to locate the positions of the mercury meniscus (Carnazzi 1903; Richards & Stull 1903;

Dolezalek & Speidel 1920). Both Richards & Stull and Carnazzi used Amagat's value for the compressibility of glass; Bridgman (1925) has shown that the compressibility of glass varies widely according to its silica content, and consequently large errors may have been introduced into their work.

Metals are very much more consistent in their elastic behaviour than glass and, since they have a smaller compressibility, the correction for the change in volume of the piezometer is correspondingly smaller. Bridgman (1909, 1911*b*) used iron, Richards & Brink (1907) both copper and iron, and Smith & Keyes (1933) nickel piezometers to measure the compressibility of mercury. Since Smith & Keyes (1933) made measurements at temperatures up to 300°C, they had to calculate the distortion of the piezometer from the elastic constants of nickel. Bridgman (1909, 1911*b*) and Richards & Brink (1907) measured the linear compressibility of their metals and assumed that they were uniformly compressible in all directions; the justification for this assumption was provided by Bridgman (1909, 1923). We have pointed out that Richards's value for the compressibility of iron was 35% too small and Bridgman's earlier measurements of the compression of mercury are in his estimation 3% too small.

In our opinion, the most reliable values for the compression of mercury may be obtained by correlating the dynamic measurements of Hubbard & Loomis (1928) with the static P - V data obtained by Bridgman (1911*b*). Gibson & Kincaid (1938) reached the same conclusion, but unfortunately they do not state how their correlation was made or give the values obtained. Bett, Weale & Newitt (1954) and Bett (1953) have shown how this may be done and have given values for the compression of mercury at 25°C, over the pressure range 0 to 3000b, which can be accurately represented by the equation

$$k_P^{25} = 4.0391 \times 10^{-6}P - 0.7817 \times 10^{-10}P^2 + 0.191 \times 10^{-14}P^3. \quad (6.10)$$

The standard deviations of the compressions are given by

$$S(k_P^{25}) = 3.9k_P^{25} \times 10^{-6} \sqrt{(P^2 + 110)}, \quad (6.11)$$

where P is the pressure in bars, gauge.

At 1000b, $S(k_P^{25}) = 1.5 \times 10^{-5}$, which corresponds to an error of $\pm 0.4\%$ of the compression at that pressure.

(iv) *Error in the density*

It is shown in § 6(c) that the uncertainty in the mean temperature of the mercury column is 0.02°C; thus, $S(T) = 0.02^\circ\text{C}$. The standard deviation of the mean coefficient of dilation of mercury and the base density of mercury have already been estimated, as $S(\bar{\alpha}) = 4.6 \times 10^{-8}/^\circ\text{C}$, and $S(\rho_0^0) = 6.0 \times 10^{-5}\text{g/cm}^3$. Using these values, together with the standard deviation of the mercury compressions calculated from equation (6.11), the standard deviation of the density of mercury at 25°C has been calculated at various pressures from equation (6.4). The results are presented in tables 4 and 5, from which it can be seen that, at atmospheric pressure, the error in the density of mercury arises principally from the uncertainties in the base density of mercury and the mean temperature of the column. Above 1000b the error is almost entirely determined by the error in the compression of mercury.

At atmospheric pressure, the density of mercury is known to one part in 170 000, but at 2500b the error has increased to one part in 10 500. These figures are based on the probability level of 68.3 %. If the maximum error in the density of mercury is taken as three times the standard deviation (probability level 97 %), the maximum error in the density at 2500b is one part in 3500.

TABLE 4. STANDARD DEVIATION OF THE DENSITY OF MERCURY AT 25° C AND PRESSURES UP TO 2500 b

pressure (bars, gauge)	$K^2S(\rho_0^0)^2$ $\times 10^8$ (g ² /cm ⁶)	$L^2S(k_T^0)^2$ $\times 10^8$ (g ² /cm ⁶)	$M^2S(\bar{\alpha})^2$ $\times 10^8$ (g ² /cm ⁶)	$N^2S(T)^2$ $\times 10^8$ (g ² /cm ⁶)	$S\rho_P^{25}$ $\times 10^4$ (g/cm ³)
0	0.357	—	0.024	0.240	0.79
500	0.358	0.280	0.024	0.240	0.95
1000	0.360	4.46	0.024	0.241	2.25
1500	0.361	22.4	0.024	0.242	4.79
2000	0.362	69.8	0.024	0.243	8.40
2500	0.364	168.4	0.024	0.244	13.0

TABLE 5. COMPRESSION AND DENSITY OF MERCURY AT 25° C AND PRESSURES UP TO 2500 b

pressure (bars, gauge)	k_P^{25}	ρ_P^{25} (g/cm ³)
0	0.000000	13.53365
500	0.002000	13.56077
1000	0.003963	13.58749
1500	0.005889	13.61382
2000	0.007781	13.63977
2500	0.009639	13.6654

(b) *Density of liquid paraffin*

Since liquid paraffin B.P. is a petroleum fraction of variable composition, it was necessary to determine the density, thermal dilation and isothermal compressibility of a sample of the blend used in the standard gauge.

It may be seen from equation (4.5) that, in order to calculate the pressure drop across the column, a knowledge of the density of liquid paraffin at the mean temperature of the mercury column, 25° C, and also at the temperature of the ambient air in the laboratory (about 20° C) is required. Although the density at 25° C has to be accurately known, that at room temperature need only be known approximately, since it is a correction to a very small term. Instead of measuring the compressions at 25 and 20° C, it was found more convenient to measure them at 25 and 40° C, and to calculate the compression at 20° C from Hudleston's (1937) equation.

(i) *Compression measurements*

The method by which we have determined the compressions of liquid paraffin B.P., up to 1000b at 25 and 40° C, was similar to that employed by Adams (1931). Each piezometer, which has the form shown in figure 8, is made of Pyrex glass and was carefully annealed and pressure seasoned before use. It is closed at the top by a ground-glass stopper, having a mercury seal; from the base, a re-entrant capillary stem rises centrally inside the piezometer and is curled over at the end. The liquid to be compressed fills the

piezometer and, when pressure is applied, mercury is forced up the capillary and falls to the bottom, where it remains trapped when the pressure is subsequently released.

The general lay-out of the high-pressure apparatus has been described by Shu-lin P'eng, Sapiro, Linstead & Newitt (1938) and Newitt & Weale (1951). In these experiments, the high-pressure vessel was closed with a hard rubber Poulter packing, held in place by a steel screw-plug, and the vessel was immersed in a thermostat bath controlled to $\pm 0.1^\circ\text{C}$ and stirred by a pump. Pressure was transmitted from a hydraulic pump through an intensifier system to the bottom of the vessel. The pressure in the vessel was measured by a free-piston gauge which was correct to at least $\pm 2b$ at 1000b. The whole apparatus was filled with paraffin, which served as the pressure-transmitting medium.

To ensure that the piezometers were completely filled with the liquid paraffin under investigation, and that all air bubbles were excluded, the filling operation was carried out under vacuum. The filled piezometer was placed on a quantity of Analar grade mercury in a cylindrical steel holder, which was then immersed in the paraffin inside the high-pressure vessel. After allowing sufficient time for the piezometer and its contents to attain the thermostat temperature, the piezometer was spun by hand as it floated in the mercury. This action helped to disperse the superfluous drops of liquid paraffin from the base of the capillary, which otherwise would have caused a depression in the mercury. Gibson & Loeffler (1941) have discussed this source of error in the measurement of liquid compressions.

The hard rubber packing was pushed into the high-pressure vessel very slowly by means of a brass screw-plunger. During this operation, the return valve to the pump was open so that no pressure could be generated in the vessel. Finally, the steel plug was screwed into position. Pressure was applied to the vessel at 5 min intervals in 50b increments. This rate of increase proved slow enough to allow the heat of compression to be dissipated. The pressure was brought to within about 20b of that desired in this way and maintained at a steady value for 5 to 10 min to ensure temperature equalization. The final adjustment of pressure was then made by slowly turning a screw ram injector incorporated in the hydraulic pump.

The release of pressure was also carried out at a slow uniform rate (occupying about 4 h from a pressure of 1000b). The sequence of closing and opening valves by which the release was begun was so ordered that there was no possibility of an accidental increase of pressure.

The mercury trapped in the piezometer was washed with alcohol and anhydrous ether and weighed. The compression of the liquid paraffin is then given by

$$k^T = \frac{(V_{\text{Hg}})_0 (1 - k_{\text{Hg}}^T) + (V_P)_0 (1 - k_g^T)}{V_0} + k_g^T, \quad (6.12)$$

where k_{Hg}^T and k_g^T are the compressions of mercury and of the piezometer glass at $T^\circ\text{C}$, and the appropriate pressure. V_0 , $(V_{\text{Hg}})_0$ and $(V_g)_0$ denote respectively the volume of liquid (total internal volume of piezometer, including the capillary), the volume of mercury trapped, and the internal volume of the capillary stem at atmospheric pressure and $T^\circ\text{C}$.

The compressions of Pyrex glass at 25°C were taken from the results published by Adams & Gibson (1931), and those at 40°C were calculated, using a temperature coeffi-

cient of compressibility obtained from Bridgman's (1925) work. The values for the compressions of mercury at 25 and 40°C were obtained from Bridgman's (1911*b*) data and the results of Hubbard & Loomis (1928); the procedure used to correlate these results by Hudleston's (1937) equation has been summarized by Bett *et al.* (1954). The volumes of the piezometers and capillary stems were calculated from the weight of mercury required to fill each piezometer, including the stem, and the weight of mercury to fill the stem alone. In determining these volumes, measurements were made at 25 and 40°C, and the piezometers were filled with mercury under vacuum to ensure that no air bubbles were trapped.

The results for the compression of liquid paraffin obtained with five different piezometers at 25 and 40°C are accurately represented by the Hudleston equation:

$$\log_{10} \frac{L^2 P}{L_0 - L} = 4.710 - 0.0016T + 7.235(L_0 - L), \quad (6.13)$$

where P = pressure (bars, gauge),

T = temperature (°C),

$L_0 = \sqrt[3]{(V_0^T/V_0^{25})}$, and

$L = \sqrt[3]{(V_P^T/V_0^{25})}$.

This equation has been solved and calculated values for the compression at 15, 20 and 25°C at pressures up to 2500 b are given in table 6.

TABLE 6. COMPRESSIONS OF LIQUID PARAFFIN AT 15, 20 AND 25°C
CALCULATED FROM HUDLESTON'S EQUATION

pressure (bars, gauge)	compression of liquid paraffin			$10^4 S(k_P^{25})$
	15°C	20°C	25°C	
500	0.0260	0.0264	0.02686	3.0
1000	0.0456	0.0462	0.04692	5.4
1500	0.0614	0.0622	0.06305	7.2
2000	0.0747	0.0756	0.07658	8.8
2500	0.0862	0.0872	0.08826	10.1

The standard deviation of thirty experimentally determined compressions at 25°C from those calculated by Hudleston's equation is $\pm 1.15\%$ of the compression in the range investigated.

The compression of liquid paraffin is fifteen times greater than that of Pyrex glass at 1000 b. Consequently, a small error in the compression of glass is not very important in measurements of the compression of this liquid. Nevertheless, since the compression of glass was taken from the work of Adams & Gibson (1931) and Bridgman (1925), it was necessary to ascertain that there were no large systematic errors in our experimental method by measuring the compression of some reference substance.

Benzene was chosen as the standard substance, since it can be obtained in a pure state and its compressions over the temperature range 25 to 65°C at pressures up to 1000 b have been accurately measured by Gibson & Kincaid (1938). Bett *et al.* (1954) have shown that Gibson's compression measurements can be accurately represented by the Hudleston equation:

$$\log_{10} \frac{L^2 P}{L_0 - L} = 4.5772 - 0.00343T + 5.962(L_0 - L), \quad (6.14)$$

where P , T , L_0 and L have the same significance as in equation (6.13).

They also showed that the initial coefficients of isothermal compressibility calculated from this relationship are in excellent agreement with those calculated from reliable velocity of sound data in benzene.

The benzene used for the compression determinations was a standard sample supplied by the Chemical Research Laboratory, Teddington. Its physical properties, determined by the Chemical Research Laboratory, are given in table 7, together with the corresponding properties of the sample of benzene used by Gibson. The purity of the benzene was established by freezing-point measurements, and the density at 25° C was obtained by linear interpolation of the experimentally determined values at 20 and 30° C. The refractive index at 25° C was obtained by combining the value at 20° C with the rate of change of refractive index with temperature obtained by Forziati, Glasgow, Willingham & Rossini (1946). It can be seen from this table that the two samples of benzene are almost identical.

TABLE 7. PHYSICAL PROPERTIES OF THE CHEMICAL RESEARCH LABORATORY BENZENE COMPARED WITH THOSE OF THE SAMPLE USED BY GIBSON

physical property	C.R.L. sample	Gibson's sample
purity	99.99 ± 0.005 mol %	—
density 20° C	0.87903 ± 0.00005 g/ml.	—
25	0.87371 ± 0.00005	0.87366
30	0.86835 ± 0.00005	0.86832
refractive index n_D^{20}	1.50106 ± 0.0001	—
n_D^{25}	1.4978 ₆	1.4983 ± 0.0002

According to Black, Joris & Taylor (1948), benzene absorbs water rather readily, the solubility being 0.04 g of water in 100 g of benzene at 20° C. Great care was therefore taken to prevent contamination, when the piezometers were being filled. Figure 8 shows, in diagrammatic form, the apparatus used to fill the piezometers under vacuum.

The standard sample of benzene was supplied in a break-tip Pyrex ampoule, *A*. After opening the high-vacuum stopcocks, *D* and *C*, the apparatus was evacuated to a pressure of 10^{-4} mm. Hg. Stopcock *C* was then closed and the internal break tip broken with the electromagnetic hammer *F*. The receiver *E* containing a few grams of calcium hydride was cooled with liquid nitrogen until all the benzene had condensed into it. This receiver served as a storage vessel, the benzene being kept in the dark under its own vapour until required. A clean piezometer, its stopper lubricated with the minimum amount of Apiezon grease grade L necessary to secure a vacuum-tight seal, was placed in vessel *G* and the stopper *B* replaced. With stopcock *D* open and *C* closed, the vessel and the piezometer were evacuated to a pressure of 10^{-4} mm Hg; this took a considerable time, as the capillary tube in the piezometer has a small bore. Stopcock *D* was then closed and *C* slowly opened, so that benzene vapour from the vessel *E* at room temperature diffused throughout the piezometer and vessel *G*. When the pressure in vessel *G* had increased to the vapour pressure of benzene at room temperature, stopcock *C* was closed and *D* opened and the piezometer re-evacuated. After this had been completed, valve *D* was closed and *C* slowly opened, while vessel *G* was cooled to about 6° C. When enough benzene had collected in vessel *G* to fill the piezometer, stopcock *C* was closed and dry air was allowed to enter the vessel through stopcock *D*. This resulted in the remainder of the benzene being

sucked up into the piezometer and completely filling it. After removing the stopper *B*, the piezometer was withdrawn and the compressibility of the benzene was measured by the same procedure as for liquid paraffin.

It may be seen from table 8 that the compressions of benzene at 25 and 40°C we obtained are smaller than those calculated from equation (6.14), based on Gibson &

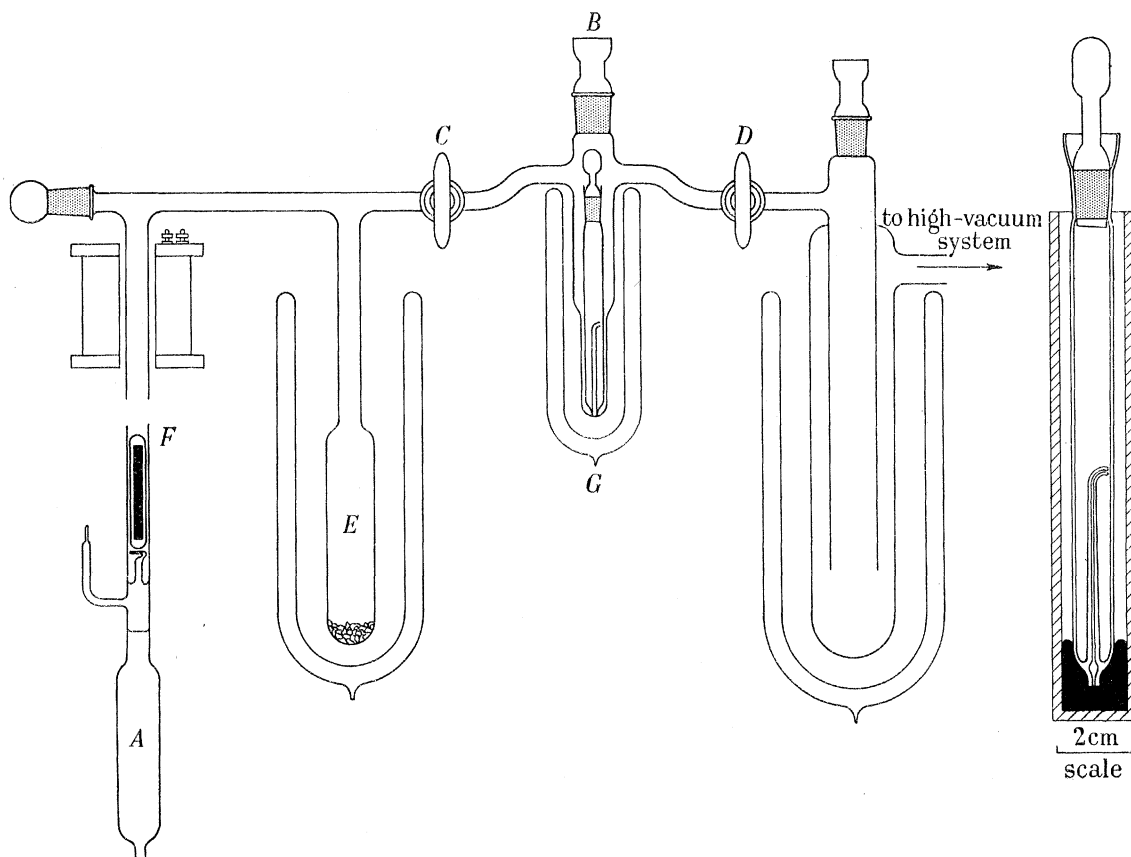


FIGURE 8. Diagram of one of the piezometers and the apparatus used to fill it with benzene under vacuum.

TABLE 8. COMPRESSION OF CHEMICAL RESEARCH LABORATORY BENZENE

pressure (bars, gauge)	temperature (°C)	compression benzene		difference $10^4(k_G - k_N)$
		Gibson	Newitt	
405.7	25	0.03262	0.03237	+2.5
811.4	25	0.05678	0.05634	+4.4
405.7	40	0.03617	0.03585	+3.2
811.4	40	0.06217	0.06181	+3.6
1014.3	40	0.07293	0.07249	+4.4

Kincaid's work. The average deviation of the results is 3.62×10^{-4} ; this corresponds to a difference in the compression of about 0.5% at 1000b and 40°C. The smallness of this error shows that the large systematic deviations for which we were looking do not exist, and we may accept the values we have obtained for the compressions of liquid paraffin as correct within the random experimental error of our determinations.

(ii) *Base density*

The density of liquid paraffin was measured at 15, 20, 25 and 40°C, by the National Physical Laboratory, Teddington. That at 25°C was found to be 0.87401 g/cm³, and the results over the temperature range 15 to 40°C may be represented to within $\pm 0.2 \times 10^{-4}$ g/cm³ by the formula

$$\sigma_0^T = 0.88017 - 6.10 \times 10^{-4}(T-15) - 4.16 \times 10^{-7}(T-15)^2, \quad (6.15)$$

where σ_0^T is the density of liquid paraffin g/cm³ at atmospheric pressure and $T^\circ\text{C}$.

Since the densities were measured to ± 0.0001 g/cm³, $S(\sigma_0^T)$ may be assumed to be less than $\pm 0.00003_3$ g/cm³.

(iii) *Error in the density*

The density of liquid paraffin at some pressure, P bars, and the mean temperature of the column, $T^\circ\text{C}$, σ_P^T , is given by

$$\sigma_P^T = \frac{\sigma_0^t}{(1-k_P^T)[1+\bar{\alpha}(T-t)]}, \quad (6.16)$$

where σ_0^t = the density of liquid paraffin at some base temperature, $t^\circ\text{C}$, and atmospheric pressure,

k_P^T = the compression of liquid paraffin at $T^\circ\text{C}$ and P bars, and

$\bar{\alpha}$ = the mean coefficient of dilation of liquid paraffin over the temperature range, t to $T^\circ\text{C}$.

If the base temperature is taken as 25°C, then

$$\sigma_P^T = \frac{\sigma_0^{25}}{(1-k_P^{25})(1+\alpha\Delta T)}, \quad (6.17)$$

where $\Delta T = (T-25)$ is the difference between the mean temperature of the column and 25°C, and

α = the true coefficient of dilation of liquid paraffin at 25°C.

Thus, from equation (6.17),

$$S(\sigma_P^T) = \sqrt{[Q^2S(\sigma_0^{25})^2 + R^2S(k_P^{25})^2 + V^2S(\Delta T)^2]}, \quad (6.18)$$

where $Q = 1/(1-k_P^{25})(1+\alpha\Delta T)$,

$R = \sigma_0^{25}/(1-k_P^{25})^2(1+\alpha\Delta T)$, and

$V = \sigma_0^{25}\alpha/(1-k_P^{25})(1+\alpha\Delta T)^2$.

Values for the density of liquid paraffin at 25°C at various pressures calculated from equation (6.17) are given in table 9. It has been shown in the preceding subsections that $S(\sigma_0^{25}) < \pm 0.00003_3$ g/cm³ and $S(k_P^{25}) = \pm 0.015k_P^{25}$, and it will be shown in § 6(c) that $S(\Delta T) = 0.02^\circ\text{C}$. Using these values for the standard deviation of the variables, the standard deviation of the density of liquid paraffin at 25°C, given in table 9, has been calculated from equation (6.18). It may be seen from this table that, as in the case of mercury, the errors in the base density and mean temperature of the column contribute very little towards the standard deviation of the density of liquid paraffin at pressures above atmospheric. Although the density at atmospheric pressure is known to about 1 part in 25 000, the error increases to 1 part in 3000 at 500b and to 1 part in 1000 at 2000b.

TABLE 9. STANDARD DEVIATION OF THE DENSITY OF LIQUID PARAFFIN AT 25° C AT PRESSURES UP TO 2500 b

pressure (bars, gauge)	σ_p^{25} (g/cm ³)	$Q^2S(\sigma_0^{25})^2$ $\times 10^8$ (g/cm ³) ²	$R^2S(k_p^{25})^2$ $\times 10^8$ (g/cm ³) ²	$V^2S(\Delta T)^2$ $\times 10^8$ (g/cm ³) ²	$S(\sigma_p^T)$ $\times 10^4$ (g/cm ³)
0	0.87401	0.111	0.00	0.015	0.35
500	0.8981	0.12	8.18	0.02	2.9
1000	0.9170	0.12	27.00	0.02	5.2
1500	0.9328	0.13	51.37	0.02	7.2
2000	0.9465	0.13	81.36	0.02	9.0
2500	0.9586	0.13	112.76	0.02	10.7

(c) *Mean temperature of the column*

In calculating the error in the density of mercury and liquid paraffin at various pressures, it was assumed that the mean temperature of the mercury column and oil return line is controlled at $25 \pm 0.02^\circ \text{C}$. In order to attain such a constant temperature, both the column and return line are enclosed in a well-lagged water jacket, through which water is circulated from a thermostatically controlled tank.

With reference to figure 9, the water jacket, 28 ft. long, is made of 6 in. diameter brass tube, built up of three flanged sections. The end flange of the bottom section is bolted to a square brass plate, which in turn is supported on the base-plate by four steel pillars, so that the jacket terminates some 7 in. above the end-block at the bottom of the mercury column. At the top of the column, the water jacket is extended to the top of the end-block by enlarging the diameter of the jacket to 10 in. over the last foot of its length. The jacket is lagged along its entire length with 2 in. thick sections of preformed cork slabs, which are held in position by a polished aluminium casing. In order that the joints in the mercury column and return line may be periodically inspected, two pairs of sight glasses are located in the jacket at the appropriate points.

A rectangular galvanized iron tank of 60 gal. capacity, lagged on its four sides with 2 in. of cork, serves as a constant-temperature reservoir. To secure efficient agitation of its contents, a horizontal baffle is fixed about 4 in. from the bottom of the tank, so that it touches two of the sides, but clears both ends by about 3 in. A short length of 5 in. diameter brass tubing has been fixed in the centre of the baffle, so that its axis is at an angle to the vertical. A stainless steel propellor, driven directly by a $\frac{1}{4}$ h.p. electric motor, forces the water down the pipe and round the baffle. This arrangement reduces the 'dead space' and the vortices in the tank, with consequent increase in the efficiency of agitation. The water is heated by two 1150 W immersion heaters, *A*, which are inserted in one end of the tank just below the baffle, where the velocity of the water is high, and the temperature control is provided by a mercury-toluene thermostat, *B*, operating in conjunction with a relay. In order to reduce 'hunting', a carbon filament lamp, *C*, connected in parallel with the immersion heaters, is placed near the thermostat, the distance between the two being adjusted so as to give an on/off cycle of about 25 s duration.

Water is withdrawn from one end of the tank by means of a gear pump, *D*, connected to a $\frac{1}{4}$ h.p. electric motor, and pumped along a well-lagged $\frac{1}{2}$ in. diameter copper pipe to the top of the column. After flowing down the column, it is returned to the tank through an outlet situated at the bottom of the jacket; the maximum rate of flow, 160 gal./h, may be reduced if necessary by adjusting valve *E*, while valve *F*, located in the outlet pipe,

determines the water level in the jacket. The variation in the speed of pumping caused by slight fluctuations in the mains voltage necessitates some device to ensure that the level remains constant. Since the temperature of the mercury column is estimated from the mean temperature of the water as it enters and leaves the jacket, any control that switches the

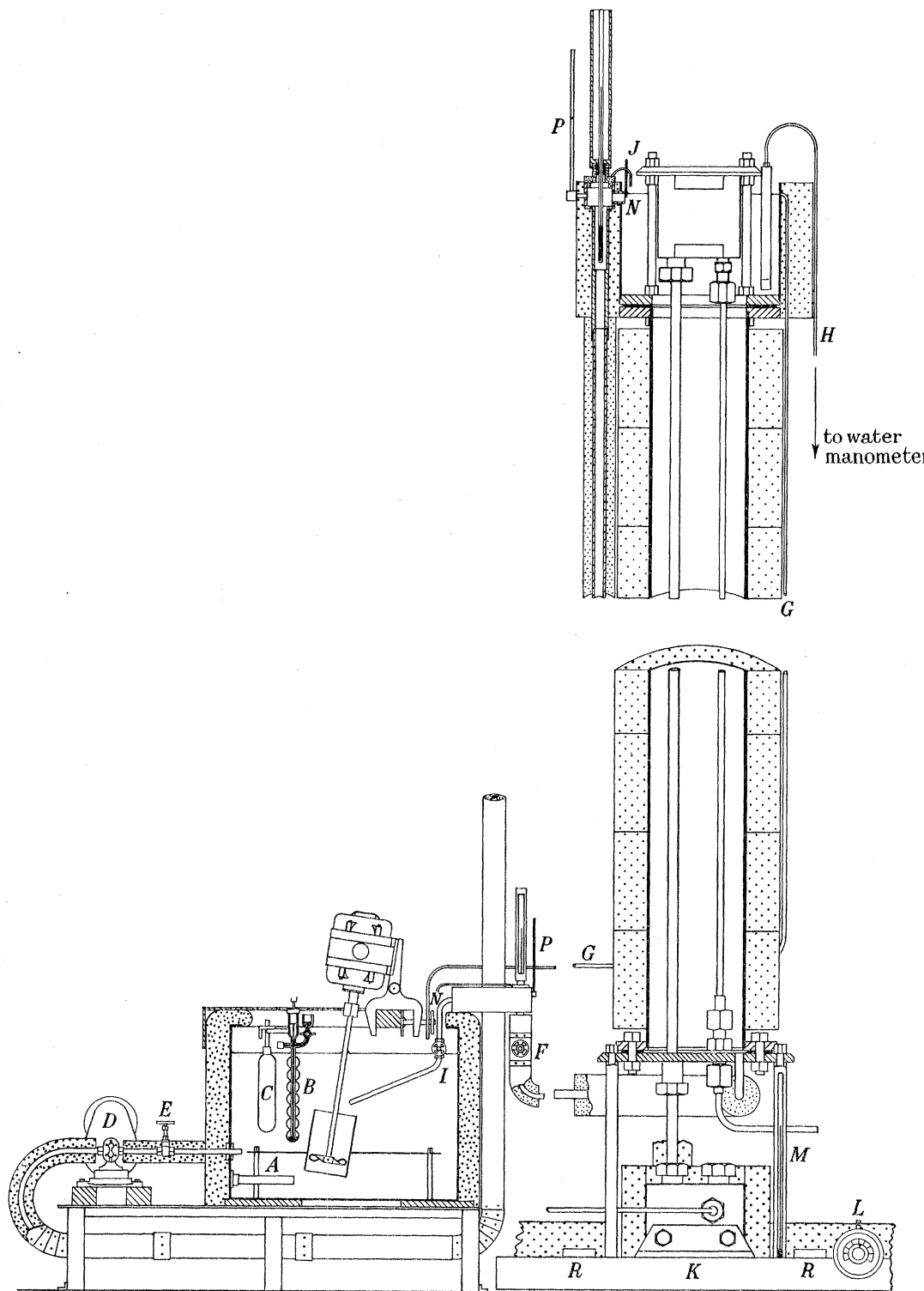


FIGURE 9. Diagram of the apparatus used to maintain and measure the mean temperature of the mercury column.

pump on and off is undesirable, as it will upset the thermal equilibrium of the system; consequently, an overflow pipe, G , $\frac{1}{4}$ in. in diameter, is inserted in the water jacket about 1 in. from the top. The water level indicated by a pneumatically operated water gauge, H , situated at the base of the column, can be adjusted by valve F so that water just trickles down the overflow pipe into the thermostat tank. Any small fluctuations in the rate of pumping then result in a corresponding variation in the rate of discharge through the overflow, while the water level, determined by the position of the overflow pipe, remains constant.

Since the water jacket terminates above the lower end-block, provision has been made for preventing the conduction of heat away from the mercury column to the large cast-iron base-plate K . Four 100 W electric heaters, R , are symmetrically clamped to the base-plate, the temperature of which is controlled to within $\pm 0.05^\circ\text{C}$ of the temperature of the water leaving the jacket, with the aid of a bimetallic thermostat, L , working in conjunction with a hot-wire relay. The temperature of the base-plate is measured by the mercury-in-glass thermometer M , the bulb of which rests in a mercury cup drilled in the base-plate, while the thermostat is held in a brass pocket so designed that it has a large surface area in contact with the plate. The exposed mercury and oil return line, end-block and base-plate are all well lagged, using preformed and granulated cork.

Two solid-stem mercury-in-glass thermometers, graduated in 0.01°C , over the range 24 to 26°C , are used to estimate the temperature of the water as it enters and leaves the jacket. These thermometers are fixed into pockets which are situated as near to the inlet and outlet of the jacket as practicable and are so designed that the velocity of the water past the bulb is as high as possible without seriously reducing the flow through the jacket. It is estimated that the response lag for a velocity of 5 ft./s achieved during normal operation is less than 3 s. The weir, J , and the valve, I , placed on the downstream side of the upper and lower pockets are adjusted so that water trickles out of the vents, N , in the top of the pocket, thus ensuring that the thermometers are immersed to a known graduation. However, care must be taken to see that any such adjustment does not greatly increase the hydrostatic pressure on the bulb of the thermometers or erroneous temperatures will be recorded. A water manometer, P , connected to the top of each thermometer pocket, indicates by how much the pressure is in excess of atmospheric; it is found that a pressure of less than 10 cm of water-gauge is sufficient to displace all the air from the top of the pockets and cause water to discharge continuously from the vents.

The two thermometers were calibrated against the international temperature scale at seven points over the temperature range 24 to 26°C by the National Physical Laboratory. These calibrations were carried out with the thermometers immersed to the same depth as in the thermometer pockets. The standard deviation of the true temperature from the thermometer reading was $\pm 0.017^\circ\text{C}$ for one thermometer and $\pm 0.009^\circ\text{C}$ for the other, the maximum error of the calibrations being $\pm 0.005^\circ\text{C}$. Since the effect of an additional 10 cm water-gauge pressure on the bulbs of the thermometers causes an error in the temperature measurement of less than 0.001°C , and the correction for the change in the mean temperature of the air surrounding the exposed thermometer stem is only about 0.003°C , both these corrections may be neglected. Measurements of the ambient air temperature at various points along the column lead us to believe that the heat loss

represented by a temperature drop of about 0.1°C is approximately uniform. Thus, the mean temperature of the column when thermal equilibrium has been established is given by the mean of the inlet and outlet water temperatures; and the maximum error of the mean temperature so calculated is $\pm 0.01^{\circ}\text{C}$.

If mercury is compressed adiabatically, its temperature increases by $0.025^{\circ}\text{C}/b$ at atmospheric pressure and 25°C ; with liquid paraffin, the increase is about three times as large. In practice, the compression will be semi-adiabatic and, since the rates of heat transfer between these liquids and the steel tubes are very small, it is important to ensure that, after any pressure change has taken place, sufficient time is allowed for the column to approach thermal equilibrium. If this condition is observed, the maximum error in the determination of the mean temperature of the mercury column and oil return line may be assumed to be less than $\pm 0.02^{\circ}\text{C}$.

(d) *The height of the mercury column*

The walls of the mercury column may stretch both elastically and permanently under the influence of internal stresses; and it is, therefore, necessary to determine the height of the mercury column at 25°C , as a function of pressure and to check the values frequently.

The vertical distance between the two mercury menisci, which determines the height of the column, has to be measured by reference to the distance between two external points on the column. The measurement is made with an Invar tape, suitable arrangements being made for a horizontal transfer from each reference point to the tape.

Figure 10 shows the arrangement of the apparatus for making these transfers and for measuring the height of the mercury in steel column.

The insulated plugs, *A*, holding the electrodes which make contact with the mercury surfaces are based on a form of construction that has been widely used in previous high-pressure work (Newitt 1940). The bottom of the silver steel electrode is tapered to a sharp point, while a steel ball, *B*, secured by a small brass retaining cap is mounted on the top of the electrode. Before the plugs were finally secured into their seatings, the overall length of each electrode was measured from the point to the top of the ball. Assuming that the electrodes are set vertically in the end-blocks, the problem of measuring the length of the column resolves itself into a determination of the vertical distance between the top of the two steel balls.

An Invar tape, *C*, of section 0.25×0.02 in., is secured at its upper end to an Invar steel rod, *D*, held in a gymbal suspension, *E*. The rod is turned to a larger diameter at its upper end, so that it is able to support on two small studs projecting from the top of the rod, one end of a level carrier; the other end of the carrier is placed on the steel ball of the top electrode. The carrier consists of a piece of flat polished steel under which a brass weight is slung, the precision level resting on the top of the carrier. The level is retained in position by means of small pieces of angle brass and the weight below the carrier serves to lower the centre of gravity, so increasing the stability of the combined level and carrier. Reference to figure 4, plate 5, shows the level and carrier in position at the top of the column. The Invar rod may be moved up and down by means of a knurled adjusting screw, *F*, so that, with the aid of the level, it is possible to bring the top of the electrode into the same horizontal plane as the top of the studs on the end of the rod. The tape is designed

to define a nominal distance of 29 ft. 7.75 in. (903.60 cm) when suspended vertically with an oil-damped bob of effective weight 3680 g attached to the lower end. The zero graduation is situated near the top of the tape, while, at the bottom, a scale 2 in. long is engraved in 0.01 in. intervals around the line marked 29 ft. 7.75 in. As Invar is subject to marked

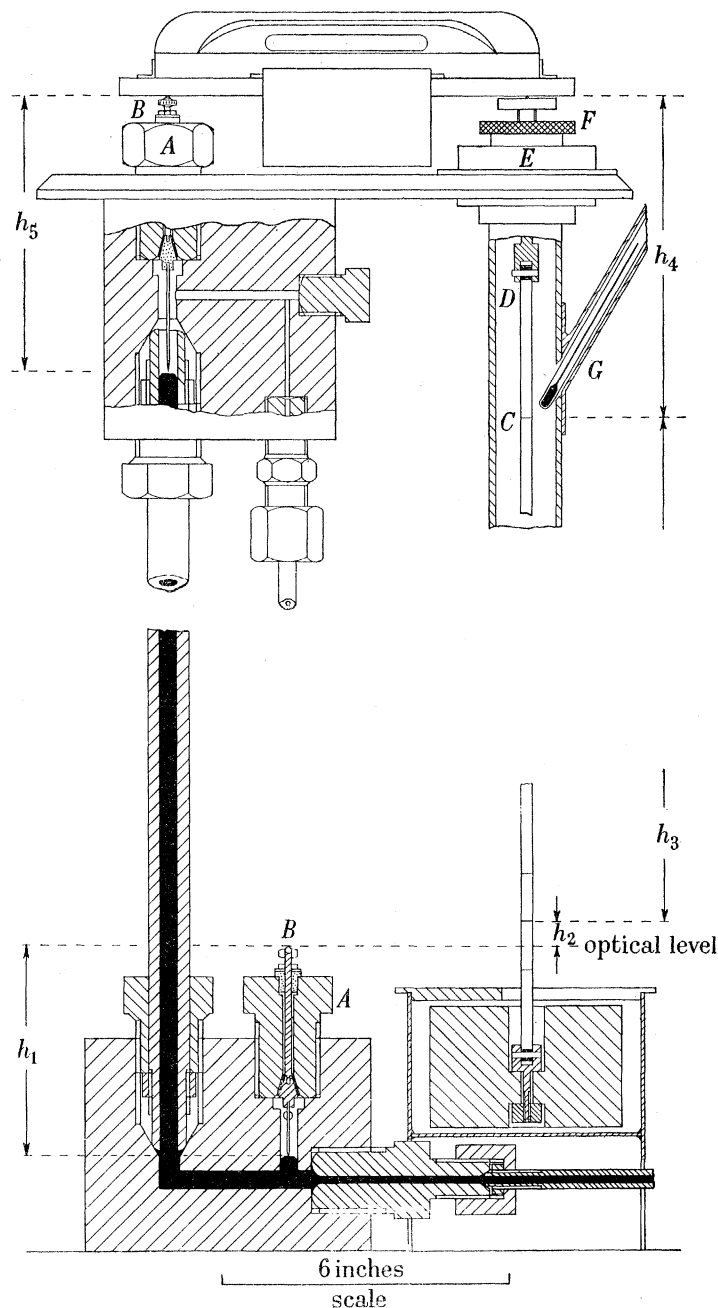


FIGURE 10. Diagram of the apparatus used to measure the height of the mercury column.

creep under tensile stress, it is important to relieve the load on the tape when it is not in use; this can be done by lowering the tape by means of the adjusting screw, F , until the bob rests on the bottom of the dash-pot. It is estimated that the tape will undergo an extension of about 4 parts per million per annum when unloaded; consequently it is important that it should periodically be recalibrated. The distance between the zero of

the tape and the top of the studs on the Invar rod was accurately measured with a cathetometer.

At the lower end of the column, the equipment, shown in figure 6, plate 5, consists of a horizontal rotary table, mounted on three levelling screws and carrying on its upper surface a 35 in. fixed focus optical level. The table is arranged so that the microscope can first be focused on to the top of the ball, then on to the edge of the tape, the whole assembly being placed so that the microscope objective is equidistant some 14.5 in. from the tape and the top of the electrode. The optical level incorporates a vernier graticule in the eye-piece, engraved so as to subdivide the divisions at the bottom of the tape into 0.001 in.

A 1 in. diameter aluminium tube is fixed to the under side of the plate supporting the gymbal suspension, and extends almost to the graduated scale at the bottom of the tape. As well as preventing damage to the tape, this tube minimizes the effects of draughts and temperature variations in the laboratory. The mean temperature of the tape can be estimated by means of three thermometers, G , set in the side of the tube at various points along its length; the height of the mercury in steel column, H (see figure 10), is given by

$$H = h_1 + h_2 + h_3 + h_4 - h_5 - h_3\alpha(t'' - t'), \quad (6.19)$$

where h_1 = overall length of bottom electrode,

h_2 = distance from the centre graduation to the one under consideration,

h_3 = distance from the centre graduation to the zero on the tape at temperature t'' ,

h_4 = distance from the zero on the tape to the top of the Invar rod,

h_5 = overall length of the top electrode,

α = mean linear coefficient of thermal expansion of Invar,

t'' = temperature at which the tape was calibrated, and

t' = mean temperature of the tape.

The standard deviation of the length of the mercury column may be calculated from

$$S(H) = \sqrt{[S(h_1)^2 + S(h_2)^2 + S(h_3)^2 + S(h_4)^2 + S(h_5)^2]}, \quad (6.20)$$

where $S(h_1)$, $S(h_2)$, etc., are the standard deviations of h_1 , h_2 , etc. The overall lengths of the top and bottom electrodes at atmospheric pressure, h_5 and h_1 , were measured by a vernier micrometer, the standard deviation of the measurements being ± 0.005 cm. The distance from the centre graduation to the zero line on the tape, h_3 , was measured by the National Physical Laboratory to ± 0.00125 cm and the terminal scale, h_2 , was found to be accurate to ± 0.00075 cm. Although these figures are, no doubt, based on a probability level greater than that associated with the standard deviation, we have assumed that they represent the standard deviation of h_3 and h_2 . The distance from the zero line on the tape to the top of the Invar rod was measured with a vernier cathetometer, the standard deviation of the observations being ± 0.01 cm. This error is larger than any of the others, although as many as thirty observations were made, because of the difficulties associated with measurements between an engraved line and a solid edge.

Inserting these deviations in equation (6.20),

$$\begin{aligned} S(H) &= \sqrt{[(0.005)^2 + (0.00075)^2 + (0.00125)^2 + (0.01)^2 + (0.005)^2]}, \\ &= 1.23 \times 10^{-2} \text{ cm.} \end{aligned} \quad (6.21)$$

In addition to these random experimental errors, there are other errors which must be taken into account before a true estimate of the accuracy with which the length of the column is known can be made.

It is important that the current passed across the mercury-oil interface is small, otherwise emulsification of the oil takes place and reproducibility of the contact is lost; consequently use is made of an electronic relay which will operate with the extremely low input of a few microamps and handle a relatively large output current. Two argon-filled thyratrons amplify the current passing across the interfaces to light two neon lamps and so provide visual indication of contact between the mercury interface and the electrode. Preliminary experiments were performed to determine the merits of electrodes made of various metals, and it was found that silver steel gave the most promising results. Reproducibility of contact was consistently attained to ± 0.0025 cm and skin effects as the mercury surface made and broke contact were not apparent.

Possible systematic errors may arise from the contraction in length of the electrodes under pressure, and they will also occur if the electrodes are not set vertically in the end blocks. The contraction in length of that part of the electrode subjected to hydrostatic pressure is only 0.1×10^{-5} cm/b in the case of the top electrode and about half that figure for the other; thus the error may be neglected in comparison with the uncertainty in the length of the electrodes. It has been calculated that the angular deviation required to produce an error of 0.005 cm, the standard deviation of the length of the electrode, is 3° . Since it is very unlikely that the angular deviation will be of this magnitude, this error may also be neglected.

The optical level at the base of the column and the precision level at the top have a finite sensitivity. It may be calculated that the maximum error incurred during the levelling operations is ± 0.0030 cm with the optical level and ± 0.0011 cm with the precision level.

Finally, another error may arise if the capillary depression is different in the two limbs of the manometer. Although the diameters of the two oil-mercury interfaces are the same, the shape of the menisci may vary slightly as the pressure is increased, because of the effect of pressure on the interfacial surface tensions. Since the difference in pressure between the top and the bottom of the column is only about $11.4b$, the difference in shape between the two menisci, which is the important factor, may be assumed to be very small and hence the error negligible.

The random error in the measured height of the mercury column arising from errors in the reproducibility of contact and finite sensitivity of the levels is 0.48×10^{-2} cm. Hence, the total standard deviation is 1.32×10^{-2} cm. This error corresponds to an error in the height of the mercury-in-steel column of one part in 70 000.

(e) *Acceleration due to gravity*

The absolute value for the acceleration due to gravity at the National Physical Laboratory, Teddington, was determined by Clark (1939) as 981.1815 cm/s². This value was subsequently slightly amended by Jeffreys (1949) to 981.1832 cm/s², with a standard error of ± 0.0006 cm/s².

A value, at the Imperial College of Science and Technology, may be calculated from this by the application of small corrections for latitude and altitude, but the result may

be in error because of local anomalies of isostasy or topography. In order to obviate this error, the value of the acceleration due to gravity at the two stations must be compared by some form of gravimeter. By this method, the value at the Geological Survey base, South Kensington, was found to be 0.00704 ± 0.00005 cm/s² greater than the value at the National Physical Laboratory. During the course of a gravitational survey of Kent, carried out by the Department of Geophysics of the Imperial College, the value at the College base was found to be 0.00179 ± 0.0005 cm/s² less than that at the Geological Survey base (Afshar 1950). Hence, the absolute value of the acceleration due to gravity at the Imperial College base, longitude $0^\circ 10' 23''$ W, latitude $51^\circ 29' 54''$ N, and altitude 20 ft. above mean sea-level, is 981.1867 ± 0.0008 cm/s².

The 'free-air' correction for the rate of change of the acceleration due to gravity with altitude is -0.000094 cm/s² ft. Thus, if allowance is made for the difference in elevation between the base station and the pressure standard, the value of the acceleration due to gravity at the mid-point of the mercury column is 981.184 ± 0.001 cm/s², and that at the level of the free-piston gauges is 981.185 ± 0.001 cm/s².

(f) *Subsidiary hydrostatic heads*

In developing the equation used to calculate the pressure drop across the column, it was assumed that the apparatus is free from air, and that all the pipe-lines and equipment outside the water jacket are at the same temperature as the ambient air in the laboratory. Care was taken when filling the apparatus with oil and mercury to ensure that no air was trapped. Now, consideration will be given to the temperature distribution along the unlagged pipe-lines used to transmit the pressure from the top and the bottom of the column to the two pressure balances.

The two oil pipe-lines connecting the column to the ancillary equipment are fixed horizontally, and as closely together as possible, to the walls of the laboratory. Thus, the temperature gradients in the oil, caused by the pipe-lines cooling from the temperature of the water jacket to that of the laboratory, do not affect the hydrostatics of the system, since they occur in horizontal sections of the pipe-lines which are 15 ft. long. Both pipe-lines then rise vertically to a height of about 5 ft. and are connected to their respective oil bottles at the top of the bench, and it is at this point that the two lines are separated. However, the bench is so arranged that the pipe-lines connecting the bottles to the pressure balances are as symmetrical as possible, so that if any change in the temperature of the laboratory occurs, the temperature gradient is the same in both pipe-lines, and the net effect on the pressure difference is zero. Since two of the walls of the laboratory in which the foot of the mercury column and the ancillary equipment is installed serve as retaining walls for large water reservoirs, the mean ambient air temperature is remarkably constant throughout the year.

The only subsidiary hydrostatic head which has to be known in order to calculate the pressure drop across the column is the difference in elevation between the piston and cylinder assemblies in the two free-piston gauges. The base of each gauge is fitted with three levelling screws which rest on an iron plate firmly fixed in concrete. Thus, if the position of each piston and cylinder assembly is observed through a cathetometer, it is possible to ensure that they are at the same elevation by adjusting the levelling screws

on one or the other balance. It is estimated that the maximum difference in elevation of the two piston and cylinder assemblies, when the gauges are levelled in this manner is ± 0.3 cm. Thus, the standard deviation may be assumed to be ± 0.1 cm.

(g) *Standard deviation of the pressure difference across the column as a function of pressure*

It has been shown in § 4 that

$$\Delta P = g[H(\rho_{P_M} - \sigma_{P_B})^T + h_e \sigma^t].$$

Since the height of the mercury column, H , the density of mercury, ρ , and the density of liquid paraffin, σ , vary with pressure, the pressure difference across the column, ΔP , is also a function of pressure. The increase in the pressure difference is less than 0.3% over the pressure range 0 to 2000 b; thus, an assessment of the standard deviation in the pressure difference may be made, using the equation

$$S(\Delta P) = \sqrt{[A^2 S(\rho^T)^2 + B^2 S(\sigma^T)^2 + C^2 S(H)^2 + D^2 S(g)^2 + E^2 S(h_e)^2]}, \quad (6.22)$$

in which, $A = (\partial \Delta P / \partial \rho^T)$, $B = (\partial \Delta P / \partial \sigma^T)$, etc., are evaluated at a mean pressure of 1000 b.

Each of the terms in equation (6.22) has been computed at various pressure levels from the standard deviations of the variables previously estimated. The results are presented in table 10.

The standard deviation of the pressure difference across the column may be represented as a function of pressure by the equation

$$S(\Delta P) = 2.05 \times 10^{-4} + 2.24 \times 10^{-7} P + 1.158 \times 10^{-10} P^2, \quad (6.23)$$

where P and $S(\Delta P)$ are measured in bars.

TABLE 10. STANDARD DEVIATION OF THE PRESSURE DIFFERENCE ACROSS THE COLUMN AT MEAN PRESSURES UP TO 2500 b

pressure (bars, gauge)	$AS(\rho^T)^2$ $\times 10^8(\text{b}^2)$	$BS(\sigma^T)^2$ $\times 10^8(\text{b}^2)$	$CS(H)^2$ $\times 10^8(\text{b}^2)$	$DS(g)^2$ $\times 10^8(\text{b}^2)$	$ES(h_e)^2$ $\times 10^8(\text{b}^2)$	$S(\Delta P)$ $\times 10^4(\text{b})$	$\frac{100 S(\Delta P)}{\Delta P}$ (%)
0	0.50	0.10	2.69	0.01	0.81	2.02	0.0018
500	0.73	7.73	2.69	0.01	0.81	3.46	0.0030
1000	4.08	23.4	2.69	0.01	0.81	5.56	0.0049
1500	18.5	41.7	2.69	0.01	0.81	7.97	0.0070
2000	56.8	62.3	2.69	0.01	0.81	11.0	0.0097
2500	136	85.0	2.69	0.01	0.81	15.0	0.0132

The standard deviations of the height of the mercury column, the acceleration due to gravity, and the difference in height of the two piston and cylinder assemblies are independent of pressure. Of these three sources of error, the uncertainty in the measurement of the height of the mercury column contributes the most towards the error in the pressure difference across the column, and, at pressures below 200 b, it is the controlling factor. Above 500 b, the errors in density of liquid paraffin and mercury provide the largest contribution towards the combined error. Both these errors are functions of pressure; the former is the more important at pressures below 2000 b, but the latter is the controlling factor above this pressure.

The coefficient of variation of the pressure difference of approximately 11·36 b across the column is 0·0030 % at 500 b (one part in 32 800), 0·0070 % at 1500 b (one part in 14 300) and 0·0132 % at 2500 b (one part in 7600).

7. ERROR ARISING FROM A PRESSURE TRANSFER

(a) *Introduction*

The simplest form of free-piston gauge consists of a uniform cylindrical piston that has been lapped to fit closely into a cylinder block. The exactitude of the fit is a compromise in which the difference in diameter of the piston and cylinder must be large enough to prevent sticking caused by deviations from axial symmetry and yet small enough to avoid excessive leakage of fluid past the piston.

The gauges used to transfer the pressure from the bottom to the top of the column must be capable of accurately reproducing pressures from about 10 to 2500 b. In practice, it is very difficult to design a gauge that is uniformly sensitive over such an extended pressure range; if the piston is large enough to give accurate results at low pressures, both the oil leakage past the piston and the number of weights required to balance the pressure become excessive at high pressures. In order to overcome these difficulties, free-piston gauges are used in which piston and cylinder assembly may be changed to suit the pressure range under investigation.

(b) *Description of gauges*

Figure 11 shows in diagrammatic form one of the free-piston gauges used in conjunction with the column. The valve block of Vibrac steel carries on one side a high-pressure valve, *A*, similar to those used throughout the rest of the apparatus and on the other side a standard high-pressure connector, *B*, the inner end of which forms a seating for the valve spindle. The block is mounted on a cast gun-metal base, *C*, supported on three levelling screws and carrying a circular spirit level. On the top of the block a male connector with a domed seating has been machined, on to which is screwed a central support column made of Vibrac steel and bored $\frac{1}{4}$ in. diameter throughout its length. The various piston and cylinder assemblies can be screwed into the 1 in. B.S.P. flat-bottomed seating at the top of the column. Each piston of hardened steel has been ground and lapped to fit closely into a cylinder block, the vertical movement being confined by the acorn head, *D*, at the top of the piston and the cylindrical stop at the bottom. The thrust from the piston is transmitted via a $\frac{1}{4}$ in. diameter steel ball seated in the acorn head to the stainless steel weight-carrier where it is balanced by loading the carrier with circular cast-iron weights.

Each set of weights consists of nineteen disks, eleven having a nominal mass of 6665 g, two of 2666 g, and one of 1333 g. Five smaller disks, two of 666·5 g, two of 266·6 g, and one of 133·3 g, are made of mild steel, while a box of standard analytical weights furnishes weights of a smaller denomination. The largest disks are approximately 10 in. in diameter and 0·875 in. thick, all have a machine finish and a circular hole in the centre just large enough to allow the weight to be slipped freely over the top of the carrier. Each disk is provided with a small recess in the underside which engages with a tongue machined on the top of the disk below, the bottom disk being located by the base of the carrier. Thus,

all the weights may be stacked on the carrier symmetrically; this is important as any slight eccentricity in the application of the load results in a torque which will throw the axis of the piston out of parallel with that of the cylinder.

The cast-iron disk weights are protected from atmospheric corrosion by coating them with a urea formaldehyde type of lacquer incorporating a non-volatile alkyd resin

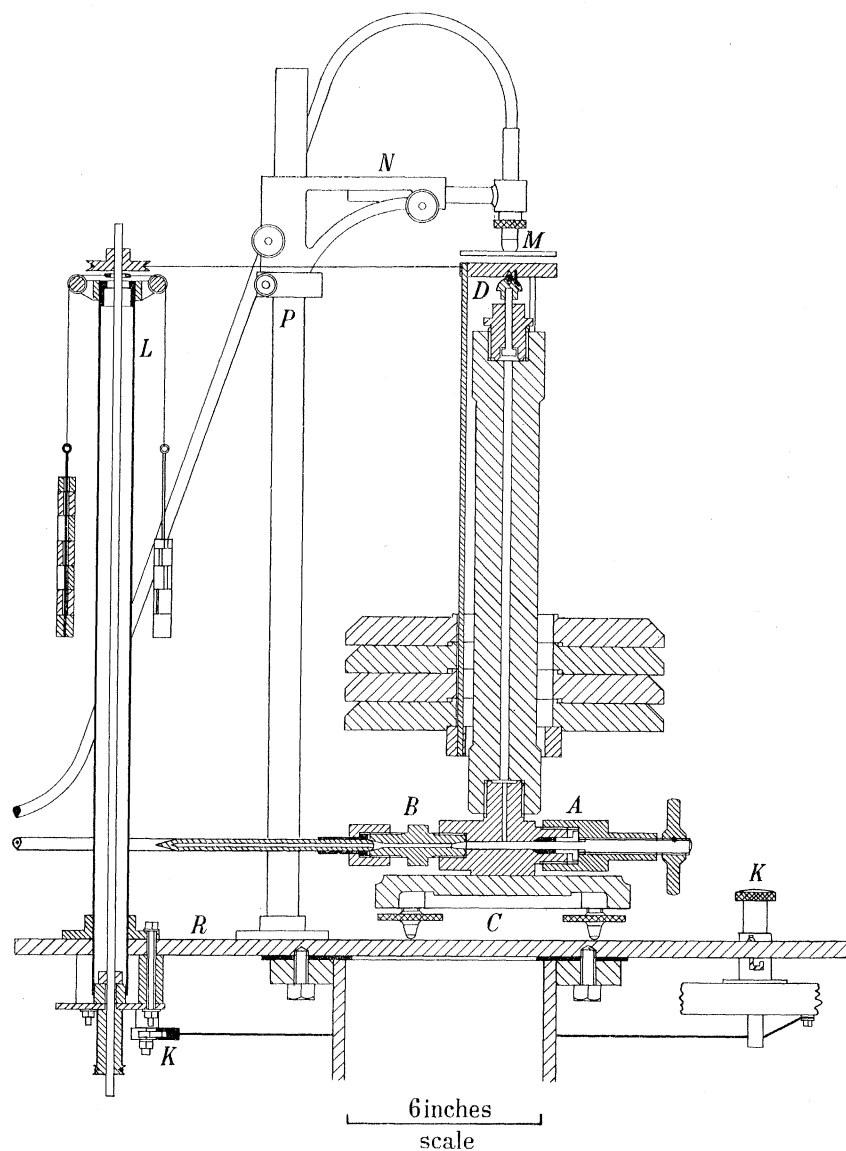


FIGURE 11. Diagram of a free-piston gauge and its accessory equipment.

plasticizer. This lacquer gives a smooth, hard, non-porous finish that does not flake or chip easily.

In order to reduce the frictional force between the pistons and cylinders, and hence increase the sensitivity of the gauges, provision has been made to rotate the pistons. A small tongue, fixed to the top of the weight-carrier, fits loosely into a groove cut in the side of the acorn head; thus, by rotating the carrier, the piston too is rotated. It is important that the tongue and groove joint be loose fitting so that, if any rocking motion is

inadvertently imparted to the carrier, it is not transmitted to the piston. As balancing the column against the two gauges takes about an hour, the pistons are rotated mechanically by means of a small constant-speed electric motor. This motor drives the shaft through a variable ratio pulley system, the carrier being rotated by a thin nylon thread which passes round both the pulley wheel at the top of the shaft and the top of the carrier. The shaft is housed in the support, L , fitted with a loose bottom bearing and, by adjusting the weights on the two pans connected to the top of the shaft, the tension in the driving thread may be reduced until it is just sufficient to keep the piston and carrier rotating. It is important to reduce this lateral force to a minimum, as it tends to pull the axis of the piston out of parallel with that of the cylinder and so to increase the frictional forces. In practice, it is found that a tension of less than 20 g is enough to keep the piston rotating at 40 rev/min, under a total load of 35 kg. While the two gauges are being mechanically rotated, they are balanced against the column as accurately as possible. Then, after the system has attained equilibrium, the top of the driving shaft is moved towards the gauge by means of a clutch, K ; this enables the nylon thread to be slipped off the top of the carrier and the final adjustment of the weight to be made while the gauges are rotating freely.

The gauges are said to be in equilibrium or 'floating' when a small change in weight causes the piston to move up or down, but as the maximum movement of the pistons is less than 0.5 cm, it is important to provide some means of ascertaining when equilibrium is established. This is done by measuring the change in capacitance between a circular electrode, M , and the top of the weight carrier, as the latter moves in a vertical direction. The a.c. bridge used has a control which enables the effective electrode capacitance to be balanced to zero when the piston is down, and its sensitivity may be adjusted to give full scale deflexion of the valve voltmeter when the piston is raised. Since the temperature of the air surrounding the electrodes and their supports is controlled to within $\pm 0.1^\circ\text{C}$, the instruments may be calibrated using a cathetometer, so that the positions of the pistons relative to the cylinders are known to 0.005 cm. This method of locating the piston has the advantage that no mechanical contact is made between the device and the carrier, hence there is no possibility of its affecting the load on the piston.

The electrode is mounted on a rigid arm, N , so that, when in use, it is vertically above the top of the carrier; in order that disk weights may be added or removed from the gauge, provision is made to swing the electrode out of position by rotating the arm about the vertical support, P . This support is fixed to the iron plate, R , set in concrete, on which the gauge rests, so that both the gauge and the electrode support are free from vibration.

Perspex cases, each fitted with a sliding front to permit access to the gauges, are used to protect them from dust. The air in the cases is heated by means of small electric heating elements fixed underneath the iron plate, R . A small electric fan circulates the air inside each case and the temperature is controlled to $20 \pm 0.1^\circ\text{C}$, by means of bimetallic thermostats.

When the gauge is in equilibrium

$$P = \frac{Wg}{A_e} + p, \quad (7.1)$$

where P is the pressure to be transferred,

p is the atmospheric pressure,

W is the total load of the piston, carrier and disk weights,

g is the acceleration due to gravity, and

A_e is the effective area of the piston, at 20°C, all measured in self-consistent units.

The accuracy with which the pressure, P , may be reproduced depends on the stability of the disk weights, the sensitivity of the balance, the constancy of the effective area and the accuracy with which the atmospheric pressure is measured. Each of these factors will now be discussed and an estimate made of the error in the pressure transfer at various pressures.

(c) *Error in the total load*

The total load on the oil surface beneath the piston, assuming that there is no friction in the piston and cylinder assembly, is made up of the load of all the weights in use together with that of the weight-carrier, acorn head, ball bearing and the effective weight of the piston.

The load of the carrier and of each of the disk weights was determined to 0.01 g, after making the necessary buoyancy correction by weighing them in air against weights of 'Class A' tolerance, which have been standardized at the National Physical Laboratory. The determinations were made by the method of double weighing using a 10 kg balance having a sensitivity of ± 0.01 g, when fully loaded. The lighter components, such as the ball bearing, acorn head and piston, were weighed to the same accuracy on an analytical balance.

The effective load of the piston is given by its weight minus the weight of oil displaced by that part of the piston submerged in the oil. Thus, the effective load is a function of the position of the piston in the cylinder. The weight of oil displaced was calculated from the volume of the submerged part. For a piston having a nominal cross-sectional area of 0.125 in.², the correction is about 0.67 g, and this correction changes by 0.074 g per mm movement of the piston. Since the position of the piston is known to within 0.005 cm, using the capacitance method of location, the correction for the weight of oil displaced may be accurately calculated.

The oil escaping from the annulus between the piston and cylinder adheres to the exposed part of the piston and to the base of the acorn head, so increasing the effective load of the piston by about 0.5 g. To reduce this error, the oil is removed periodically, while the gauge is in use, by means of a small camel-hair brush. It may be assumed that the error arising from this cause is less than 0.05 g.

In computing the buoyancy correction for the cast-iron disk weights, the density of the ambient air is derived from the expression

$$\frac{0.00129307p - 0.000004885hk}{(1 + 0.00367t) 760}, \quad (7.2)$$

where $t^\circ\text{C}$ is the air temperature,

p is the atmospheric pressure in mm of mercury at 0°C and standard gravity, namely, 980.665 cm/s²,

k is the relative humidity, expressed as a percentage, and

h is the vapour pressure of water at $t^\circ\text{C}$ in mm Hg at 0°C and standard gravity.

The protective coating applied to the cast-iron weights is slightly hygroscopic, the amount of moisture adsorbed depending on the partial pressure of water vapour in the air. The water is adsorbed slowly; for instance, if a disk of nominal mass 6665 g is removed from an atmosphere in which the partial vapour pressure of water is 17.5 mm Hg and placed in one having a vapour pressure of 9.8 mm Hg, over 4 h are necessary for the weight to attain equilibrium. The difference in weight is 0.03 g. Thus, the disks cannot be stored in dry, air-tight boxes and removed, as required, unless sufficient time is allowed for them to attain equilibrium. Consequently, it was decided to keep them in boxes exposed to the ambient air in the laboratory. The weights are weighed frequently and the weight at any particular time is obtained by interpolation. Since the diurnal variation in the partial vapour pressure of water in the atmosphere is less than 5 mm Hg, the equilibrium weight of water adsorbed may be assumed to be fairly constant and less than one part in 200 000.

The small magnetic forces introduced by using cast-iron disks and the electrostatic force between the top of the carrier and the condenser plate are constant for any given load on the carrier, and, therefore, do not affect the accuracy of a pressure transfer.

The error in the total load needed to balance a given pressure is difficult to assess accurately as it is a function of the number of weights on the carrier, but in our opinion the maximum error is not likely to exceed ± 0.3 g.

(d) *Sensitivity of the gauges*

The early users of free-piston gauges realized that the sensitivity could be increased by rotating the piston. However, little was known about the influence of the speed of rotation on the sensitivity, until Michels (1923) applied the results of Sommerfeld's treatment of friction in a lubricated journal bearing to the problem of friction in a vertical piston and cylinder assembly. He showed that, when a piston is rotated, the central position is unstable; the eccentricity of the piston increases as the speed of rotation decreases until finally, below a critical speed of rotation, solid friction appears. For the differential piston and cylinder assembly which Michels used in his investigation, the critical speed of rotation varied from 24 to 36 rev/min. Although these results are not directly applicable to the gauges under consideration, it may be assumed that there is some critical speed of rotation that must be exceeded if the gauges are to operate with maximum sensitivity. Since the central position of the piston is unstable at low speeds of rotation, other investigators have stated a preference for an oscillatory motion of the piston instead of continuous rotation. Keyes & Dewey (1927) claim that observation of the electrical resistance of the oil film between the piston and cylinder for various assemblies under actual working conditions indicates that the reversal of the direction of motion serves to restore the piston to the centre of the cylinder. If a gauge sticks at a definite point or over a small arc on the circumference of the cylinder, then the use of an oscillatory motion enables the investigator to adjust the position of the arc so as to reduce sticking to a minimum. It must be admitted, that in lapping the piston to the cylinder it is possible to produce spiral scores on the surfaces of the piston and cylinder; if such scores are present, continuous rotation of the piston will tend to screw the piston upwards or downwards depending on the direction of motion. Equally precise pressure measurements

have been obtained using both types of motion, but it was decided to rotate the pistons continuously as the driving mechanism is easier to construct. The effect of any spiral scores may be eliminated by taking the mean of two readings each time the column is balanced, the first with the gauge rotating in a clockwise direction and the second in the reverse direction.

Four sets of piston and cylinder assemblies, having nominal cross-sectional areas of 0.125, 0.05, 0.02 and 0.01 in.² are used to gauge pressures from 10 to 1500 b. Above this pressure, it is hoped to use two assemblies with a nominal area of 0.005 in.², but these have yet to be manufactured.

The sensitivity of the gauges may be measured by determining the weight required to overcome the friction force opposing the vertical motion of the piston. We have arbitrarily defined the sensitivity as the minimum increase in weight necessary to cause the piston to move from its equilibrium position at a mean velocity of 0.01 cm/min. This velocity was chosen as it is the smallest that can be conveniently estimated with the aid of the piston locating device.

When the pistons are rotating at less than their critical speed, the sensitivity of the gauges is a function of the speed of rotation, but above their critical speed it is constant. Piston and cylinder assemblies of equal nominal cross-sectional area do not often have the same sensitivity, since the gap between the two components is seldom identical. In addition, it is often difficult to obtain consistent values for a particular gauge, unless very great care is taken to ensure that no solid particles are suspended in the oil. In general, the sensitivity of each piston and cylinder assembly increases with the load on the gauge, but if the load is kept constant, the gauge with the largest piston has the greatest sensitivity.

The sensitivity of a piston and cylinder assembly with a nominal cross-sectional area of 0.02 in.² is about ± 0.2 g, when the gauge is loaded with 66 600 g (i.e. one part in 330 000). It may be assumed that, when the assemblies are used over their optimum working pressure range, the sensitivity is less than ± 0.6 g. If this uncertainty is combined with the error in the load of ± 0.3 g, discussed in the previous subsection, then the maximum error in the load transmitted to the piston face is ± 0.9 g, and hence the standard deviation may be assumed to be ± 0.3 g.

(e) *Error in the effective area*

The vertical forces acting on a stationary piston are the direct hydrostatic pressure, and the lifting force on the piston due to the viscous drag of the escaping oil. Michels (1924) has shown that, for steady efflux, provided that the piston and cylinder do not taper, half the mean clearance between the piston and cylinder should be added to the piston diameter to account for this drag.

Under high pressures, elastic deformation of the piston and cylinder takes place, owing to the local compression of the piston in both axial and radial directions and the simultaneous expansion of the cylinder. The large difference between the oil pressure at the top and the bottom of the crevice results in the cylinder being stretched more at the bottom than the top. In contrast, the base of the piston is compressed more than the top. The net result is an increase in the crevice width at the lower end of the piston and cylinder assembly. Thus the effective area of the free-piston gauge is a function of the

pressure, the vertical position of the piston in the cylinder, the mean temperature of the piston, the speed of rotation and the properties of the lubricating fluid.

The capacitance method of locating the position of the piston permits the elevation of the piston in the cylinder block to be accurately known. Thus only the effect of temperature need be considered when estimating the change in the effective area of a free-piston gauge during a pressure transfer, since all the other factors may be kept constant.

The temperature of the piston when the gauge has been rotating long enough to allow thermal equilibrium to be established depends on the ambient air temperature, the heat generated in the bearing by friction, and the cooling effect of the oil as it expands past the piston. Since the air in the cases containing the gauges is thermostatically maintained at $20 \pm 0.1^\circ\text{C}$, the true temperature of the piston will be a function of the pressure acting on the face of the piston, the speed of rotation and the tension in the drive rotating the carrier. During each pressure transfer, both the speed of rotation and the tension in the drive may be kept almost constant. Thus, providing thermal equilibrium has been established, the true temperature of the piston, and hence the effective area, will remain constant, although its value will depend on the pressure being transferred. It was considered desirable to measure the temperature difference between the piston and the ambient air under average working conditions. This had to be done by an indirect method, as it is impossible to measure the temperature of the piston directly when it is rotating. Briefly, the method used was as follows.

Two free-piston gauges were connected together and the system pumped up to the pressure at which it was desired to measure the thermal effect. One of the gauges, the right-hand one, say, was then set in motion and allowed to rotate for 3 h so that thermal equilibrium was established; the second gauge was then set in motion and the weights required to balance it against the first were noted at various intervals of time. Every precaution was taken to see that the pressure in the system maintained by the right-hand gauge remained constant and thus any change in the weights required on the second gauge was due to a change in the effective area of the gauge caused by a temperature change. Using a piston and cylinder assembly having a nominal cross-sectional area of 0.02 in.^2 , it was found that the temperature of the piston, when rotating at 40 rev/min, did not increase by more than 0.1°C at 600 b. Thus, we feel justified in assuming that the true temperature of the piston is constant to $\pm 0.2^\circ\text{C}$ during a pressure transfer.

We will assume that the standard deviation of the effective area of the piston at 20°C , $S(A)$, is given by the change in the area of the piston, ΔA , which arises from this uncertainty in the temperature.

$$\text{Thus} \quad S(A) = \Delta A = 2A\alpha \Delta T, \quad (7.3)$$

where A = the effective area of the piston at 20°C ,

$\alpha = 11.0 \times 10^{-6}/^\circ\text{C}$ is the coefficient of linear expansion of the steel with which the piston is made, and

$\Delta T = 0.2^\circ\text{C}$ is the uncertainty in the true temperature of the piston.

$$\text{Hence} \quad S(A) = 4.4A \times 10^{-6}. \quad (7.4)$$

(f) Error in the measurement of atmospheric pressure

It is sufficiently accurate to determine the atmospheric pressure to ± 0.2 mm Hg (266.6 dyn/cm^2); this is done by means of a barometer of the Fortin type.

(g) Standard deviation of a pressure transfer as a function of pressure

The total error of a pressure transfer at various pressures may be calculated from the error in the total load, the error arising from the change in the effective area of the piston and the error in the measurement of the atmospheric pressure.

Differentiating equation (7.1) with respect to each of the independent variables A , W , and p , we obtain that

$$S(T_p) \times 10^{-6} = \sqrt{\left[\left(\frac{Wg}{A^2}\right)^2 S(A)^2 + \left(\frac{g}{A}\right)^2 S(W)^2 + S(p)^2\right]}, \quad (7.5)$$

where $S(T_p)$ = the standard error of a pressure transfer at a pressure, P bars,

$S(A) = 4.4 \times 10^{-6} \text{ cm}^2$ is the standard deviation of the effective area at 20°C ,

$S(W) = 0.3 \text{ g}$ is the standard deviation of the total load transmitted to the face of the piston, and

$S(p) = 266.6 \text{ dyn/cm}^2$ is the standard deviation of the measurement of atmospheric pressure.

It may be seen from equation (7.5) that the contribution towards the standard deviation of the pressure transfer which is made by the error in the effective area is a function of the total load, W . In table 11, the error in the pressure transfer has been evaluated for the different sized piston and cylinder assemblies, assuming that the load on the gauge is 65.75 kg in each case.

TABLE 11. THE STANDARD DEVIATION OF A PRESSURE TRANSFER AS A FUNCTION OF PRESSURE

area of piston A		pressure P (bars)	$\left(\frac{Wg}{A^2}\right)^2 S(A)^2$ $\times 10^6(\text{b}^2)$	$\left(\frac{g}{A}\right)^2 S(W)^2$ $\times 10^6(\text{b}^2)$	$S(p)^2$ $\times 10^6(\text{b}^2)$	$S(T_p)$ $\times 10^3(\text{b})$
(in. ²)	(cm ²)					
0.125	0.806	80	0.133	0.124	0.071	0.57
0.05	0.323	200	0.830	0.772	0.071	1.29
0.02	0.129	500	5.21	4.84	0.071	3.18
0.01	0.0645	1000	20.8	19.4	0.071	6.34
0.005	0.0323	2000	83.1	77.2	0.071	12.65

This load represents the mean load on the gauge over the working pressure range of each piston and cylinder. We will assume that the standard deviation of the transfer of a pressure, P , is a continuous function of the pressure.

Hence
$$S(T_p) \approx 0.442 \times 10^{-3} + 6.325 \times 10^{-6}P, \quad (7.6)$$

where P and $S(T_p)$ are measured in bars.

8. COMBINATION OF THE ERRORS IN THE MEASUREMENT OF THE PRESSURE DIFFERENCES ACROSS THE COLUMN AND THE ERRORS IN THE PRESSURE TRANSFERS

It was shown in § 3 (*e*) that, for the first operation with the column,

$$P_1 = \Delta P_1 + p.$$

Thus
$$S(P_1) = \sqrt{[S(\Delta P_1)^2 + S(p)^2]}, \quad (8.1)$$

where $S(P_1)$ = the standard deviation of the pressure at the base of the column,
 $S(\Delta P_1)$ = the standard deviation of the pressure drop across the column, and
 $S(p) = 0.267 \times 10^{-3} b$ is the standard deviation of the measurement of atmospheric pressure.

For the second operation, the error in the calculated pressure at the gauge connected to the base of the column, $S(P_2)$, may be obtained from a summation of the error in the absolute pressure at the base of the column at the end of the first operation, $S(P_1)$, the error in the transfer of this pressure to the top of the column, $S(T_{P_1})$, and the error in the pressure drop across the column of the second operation, $S(\Delta P_1)$.

$$\text{Thus,} \quad S(P_2) = \sqrt{[S(P_1)^2 + S(T_{P_1})^2 + S(\Delta P_2)^2]}. \quad (8.2)$$

Hence, from equation (8.1),

$$S(P_2) = \sqrt{[S(\Delta P_1)^2 + S(\Delta P_2)^2 + S(T_{P_1})^2 + S(p)^2]}. \quad (8.3)$$

In general, the error in the measurement of the pressure at the base of the column after N operations, $S(P_N)$ is given by

$$S(P_N) = \sqrt{\{[S(\Delta P_1)^2 + S(\Delta P_2)^2 + \dots + S(\Delta P_N)^2] + [S(T_{P_1})^2 + S(T_{P_2})^2 + \dots + S(T_{P_{N-1}})^2] + S(p)^2\}}. \quad (8.4)$$

$$\text{Thus,} \quad S(P_N) = \sqrt{\left[\sum_1^N S(\Delta P)^2 + \sum_1^{N-1} S(T_P)^2 + S(p)^2 \right]}. \quad (8.5)$$

It has been shown (equation (3.4)) that

$$P_N = p + \sum_1^N \Delta P.$$

The increase in the pressure difference across the column is less than 0.3% over the pressure range 0 to 2000 b. Thus, in order to evaluate the errors in the pressure measurements, we may assume that ΔP is independent of pressure and equal to 11.36 b. If the atmospheric pressure is assumed to be 1 b, then

$$P_N = 1 + 11.36N, \quad (8.6)$$

where N is the number of operations performed with the column. If equation (8.6) is used to substitute N for P in equations (6.23) and (7.6), we obtain that

$$S(\Delta P_N) \text{ (bars)} = 2.052 \times 10^{-4} + 2.548 \times 10^{-6}N + 1.494 \times 10^{-8}N^2, \quad (8.7)$$

$$\text{and} \quad S(T_{P_N}) \text{ (bars)} = 0.448 \times 10^{-3} + 7.185 \times 10^{-5}N. \quad (8.8)$$

From equations (8.5), (8.7) and (8.8) it can be shown that

$$S(P_N) \times 10^3 \text{ (bars)} = \sqrt{(-0.13 + 0.212N + 3.014 \times 10^{-2}N^2 + 1.725 \times 10^{-3}N^3 + 1.9 \times 10^{-8}N^4 + 4.5 \times 10^{-11}N^5)}, \quad (8.9)$$

where N may have any integral value from 1 to 220.

The standard deviations of the pressure measurements have been calculated from equation (8.9) for certain values of N up to 219 and the results are presented in table 12. In the last column of the table, the coefficients of variation of the pressure measurements

are given; at 500 b, the coefficient is 0.0030 % (one part in 34 000), at 1000 and 2000 b, it is 0.0038 % (one part in 26 000) and 0.005 % (one part in 20 000).

These figures are based on the standard deviation of a normally distributed error. The probability limits of one standard deviation are 68.3 % above and below the mean; the range for accurate work of this nature is usually taken as a probability limit of 99.7 %, which is equivalent to three times the standard deviation, and the coefficient of variation should be multiplied by three.

TABLE 12. THE ACCURACY OF THE PRIMARY PRESSURE STANDARD
AS A FUNCTION OF PRESSURE

number of operations N	pressure P_N (bars)	standard deviation $S(P_N)$ (bars)	$\frac{100S(P_N)}{P_N}$ (%)
22	250	0.0061	0.0024
44	500	0.015	0.0030
66	750	0.025	0.0033
88	1000	0.038	0.0038
110	1250	0.052	0.0042
131	1500	0.066	0.0044
153	1750	0.083	0.0047
175	2000	0.101	0.0050
197	2250	0.120	0.0053
219	2500	0.140	0.0056

9. ERROR IN THE MEASUREMENT OF THE EFFECTIVE AREA OF A FREE-PISTON GAUGE

The effective area of a free-piston gauge may be calculated from the pressure at the base of the column after N operations, P_N , by the equation

$$(A_e)_{P_N} = \frac{Wg}{P_N - p}, \quad (9.1)$$

where $(A_e)_{P_N}$ is the effective area of the piston at pressure, P_N .

The standard deviation of the calculated effective area depends on the accuracy with which the pressure, P_N , the total load on the balance, W , and the atmospheric pressure is known. It may be shown from equation (9.1) that the coefficient of variation of the effective area is given by the relationship

$$\frac{100S(A_e)_{P_N}}{(A_e)_{P_N}} = \sqrt{\left\{ \left[\frac{100S(W)}{W} \right]^2 + \left[\frac{100S(P_N)}{P_N - p} \right]^2 + \left[\frac{100S(p)}{P_N - p} \right]^2 \right\}}. \quad (9.2)$$

Since the error in the load and the error in the measurement of the atmospheric pressure contribute very little towards the error in the measurement of the effective area of the piston; and since $P_N - p \approx P_N$,

$$\frac{100S(A_e)_{P_N}}{(A_e)_{P_N}} \approx \frac{100S(P_N)}{P_N}. \quad (9.3)$$

Hence the coefficient of variation of the effective area is approximately equal to that of the pressure measurement.

The alternative method of measuring the effective area of a free-piston gauge described in § 3(e) is less accurate than this method. It may be shown from equation (3.7) that, if the error in the pressure drop across the column and the measurement of atmospheric pressure are neglected, then the accuracy with which the effective area is measured is given by the accuracy with which the increase in the load ($W_2 - W_1$) is known. With a

piston and cylinder assembly having a nominal area of 0.125 in.^2 , the increase in the load on the gauge needed to balance the mercury column is about 9290 g. At 1000 b, however, when it is necessary to use a piston having an area of 0.01 in.^2 , the increase in load is only 743.2 g. The uncertainty in the load on the gauge during a pressure transfer is about $\pm 0.5 \text{ g}$, irrespective of the size of the piston or the loading. Thus, the accuracy with which $(W_2 - W_1)$, and hence the accuracy with which the effective area may be measured is very small. For instance, at 1000 b, the coefficient of variation of the effective area is 0.079 % (one part in 1265) compared to 0.0038 % (one part in 26 000) using the stepwise method of gauging the pressure.

We have discussed the error in the pressure measurements in two parts: § 6(g) dealt with the error in the calculated pressure difference across the column and § 7(g) with that in the pressure transfers from the bottom to the top of the column. It may be seen from equations (6.23) and (7.6) that, for any given pressure, the transfer error is the greater. Thus, any attempt towards improving the accuracy of the pressure measurement must first be directed towards increasing the sensitivity of the free-piston gauges and decreasing the uncertainty in the temperature of the piston.

If, at some later date, the existing free-piston gauges are replaced by more sensitive gauges, the error in the pressure difference across the column may become more important. In this event, the accuracy of the pressure measurement can only be substantially increased by a more accurate determination of the compression of mercury.

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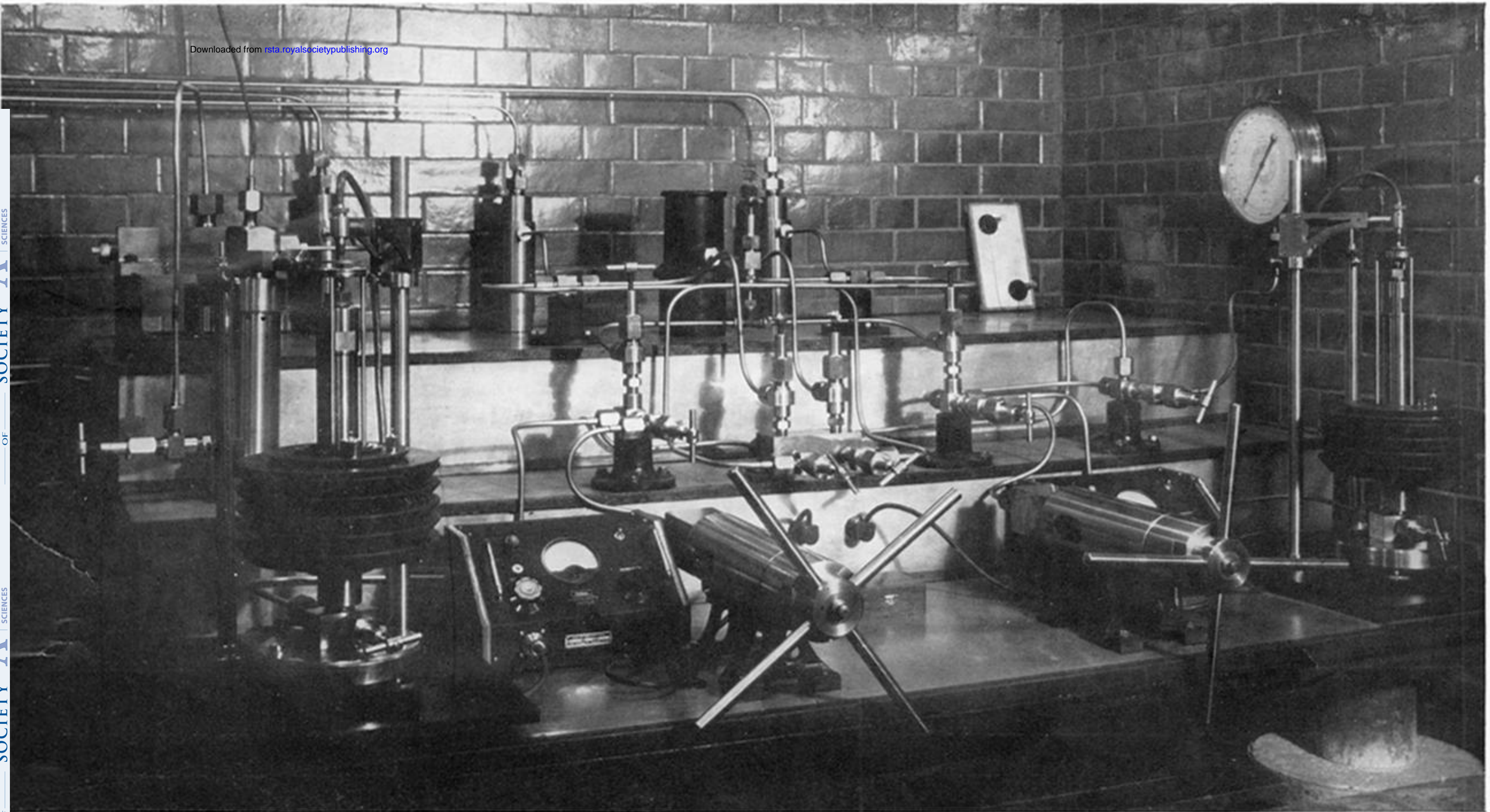


FIGURE 3. Photograph of the working bench.

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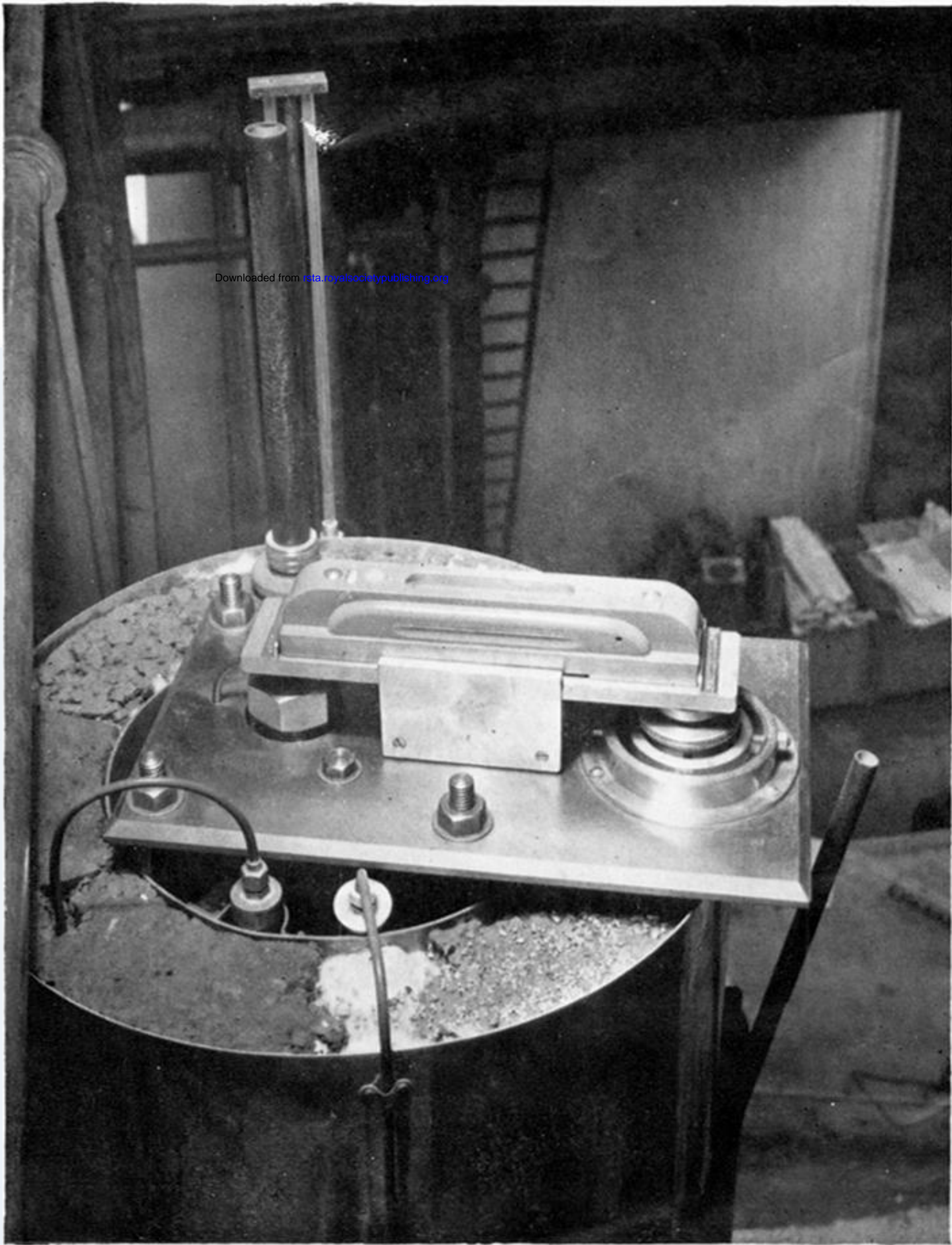
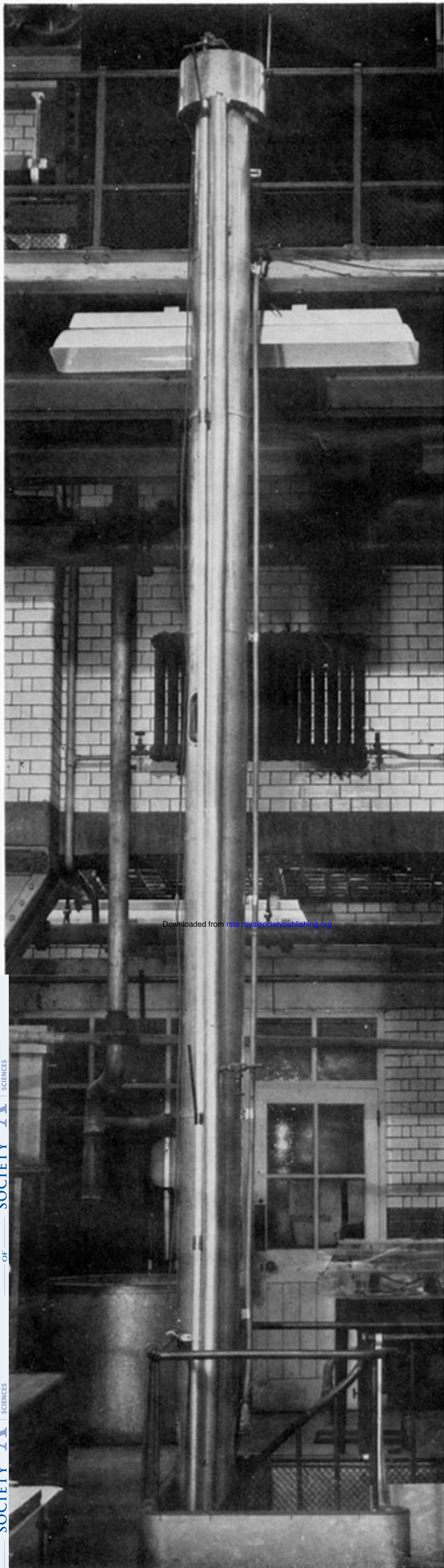


FIGURE 4. Photograph of the top of the mercury column.



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FIGURE 5. Photograph of the mercury column.



FIGURE 6. Photograph of the base of the mercury column with the lagging removed.