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## Developments in the Accurate Measurement of High Pressures

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With 7 Figures in the Text

### Abstract

The measurement of steady high pressures in a fluid system with the highest accuracy demands the use of pressure balances (free piston gauges) of accurately known effective areas. This requires a precise knowledge of the way in which the effective areas of the piston-cylinder assemblies concerned vary due to the elastic distortion caused by the applied pressure.

Two methods which have been directed to the solution of this problem are described. The first depends on a principle of similarity as applied to the deformations of two assemblies of the same general dimensions but constructed of materials having substantially different elastic moduli. The second method makes use of measurements of the flow characteristics of the pressure transmitting fluid using two pistons having a known difference of diameter.

The distortion factors are shown to be representable as linear functions of the pressure, so that the effective area at pressure  $P$  is connected with that at zero pressure by expressions of the form

$$A_P = A_0(1 + \lambda P)$$

where  $\lambda$  may be termed the distortion coefficient.

The final accuracy of the measured distortion coefficients is about  $\pm 2\%$ , which corresponds to an uncertainty in effective area of about  $\pm 1$  part in  $10^5$  at 1000 bars increasing in proportion to the pressure at higher pressures.

Some aspects of the practical calibration of pressure balances, carried out by direct balancing against assemblies calibrated by the methods described, are considered.

### 1. Introduction

The rapid development of high pressure techniques in the last few decades has given rise to considerably increased interest in the accurate measurement of high pressures, both in fundamental physics and chemistry and in the many associated industrial applications. In many thermodynamic studies, as for example the pressure-volume-temperature relations and virial coefficients of gases, the Joule-Thomson effect and the measurement of vapour pressures, the demands on accuracy are severe. Nevertheless until quite recently progress in high pressure measurement was much retarded compared with the measurement of the other thermodynamic variables, temperature and volume, and it is only within the last few years that some notable advance has been achieved. The

object of this paper is to present an up-to-date account of some recent developments at the National Physical Laboratory which have contributed to these improvements. The discussion is restricted to the case of steady pressures.

There are two quite independent basic methods by which pressures may, in principle, be measured or established, with precision, or by which other pressure-measuring equipment may be calibrated. The first, usually represented in practice by the mercury manometer or some extension of it, determines a pressure in terms of the height of a column of liquid of known density under known conditions of gravity. In the second method, pressure is measured directly in terms of the force exerted on a surface of known area. In practice this reduces to the use of the pressure balance, or free piston gauge, in which the force due to the pressure-transmitting fluid acting on the base of a cylindrical piston, free to move in an accurately matched cylinder, is balanced by a known downward force derived from calibrated masses suitably supported on the piston. The calibration of the instrument is expressed by stating the "effective area" of the piston-cylinder assembly, and owing to the distortion caused by the applied forces this quantity may be expected to vary with pressure.

In the high pressure region proper, however, the pressure balance is virtually the only instrument in the field for practical pressure measurement of the highest accuracy, as high pressure variants of the mercury manometer are very difficult to operate even for fundamental calibration purposes. Two problems therefore present themselves:

- (i) the establishment of the effective areas of suitable piston-cylinder assemblies in absolute terms at low pressures;
- (ii) the determination of the changes of effective area at higher pressures due to the distortion of the assemblies resulting from the applied pressure.

With regard to (i) details are being dealt with in other publications and we shall only summarize the present position. In the more restricted field of barometric pressure the National Physical Laboratory has for many years maintained standards based on the mercury manometer and reaching an accuracy of a few microbars (SEARS & CLARK 1933; ELLIOTT, WILSON, MASON & BIGG 1960). Recent work has shown that the effective areas of piston-cylinder assemblies based on comparison with a mercury manometer of a few atm range, and those calculated directly from diametral measurements on the components, are in agreement to within about 1 part in  $10^5$  (DADSON 1955, 1958).

The elastic distortion effect (ii) was for a long time considered to be a fundamental difficulty in the use of the pressure balance as an independent primary standard, but this situation has now been completely altered with the development



of methods by which the dependence of effective area upon pressure may be determined with considerable accuracy. The present paper deals in detail with two independent methods, termed the "similarity" and "flow" methods, recently developed at the National Physical Laboratory for this purpose.

Several early attempts to measure these distortion effects by the use of high pressure mercury manometers of various forms led to very inconsistent conclusions as to the order of magnitude of the effects to be expected (HOLBORN & SCHULZE 1915; CROMMELIN & SMID 1915; KEYES & DEWEY 1927; MEYERS & JESSUP 1931; BEATTIE & EDEL 1931). MICHELS (1923, 1924, 1932) has discussed applications to the differential type of piston-cylinder assembly. The most recent, and by far the most comprehensive, investigation of this kind is that of NEWITT and his colleagues, using a 9-m pressurised differential mercury manometer installed at the Imperial College of Science and Technology (BETT, HAYES & NEWITT 1954; BETT & NEWITT 1963). The measurements, covering a range up to 700 bars\*, were difficult, and the resulting distortion factors for six pressure balance assemblies of similar design varied among themselves by much more than would be expected from their construction. It seems that more extensive data will be necessary before a final assessment of the high pressure mercury column can be made. ROEBUCK & CRAM (1937) and ROEBUCK & IBSER (1954) have dealt with a recent development of the multiple-column type of mercury manometer covering the range up to about 200 bars.

The distortion errors of the "controlled-clearance" type of pressure balance used at the National Bureau of Standards, Washington, have been considered by JOHNSON & NEWHALL (1953) and by JOHNSON, CROSS, HILL & BOWMAN (1957); (see also BENNETT & VODAR 1963). It is hoped that the results of direct comparisons between the methods of calibration developed at the NBS and the NPL may be available in the near future. Accounts of the distortion errors of various designs of piston-cylinder assemblies from the point of view of elastic theory have also been published by ZHOKOVSKII (1960), SAMOILOV (1960), EBERT (1935, 1949, 1951) and TOYOSAWA (1963, 1964). These authors, however, give primary attention to the establishment of the distortion factors by calculation rather than by experiment. The present paper, on the other hand, describes direct experimental methods which are independent of other pressure standards, and practically independent of detailed elastic theory, to which appeal is made only in the calculation of small correction terms.

## 2. Formal Theoretical Basis

### a) General

As a basis for discussion of the methods described in this paper it is useful to develop a number of formal expressions for the changes of effective area of a piston-cylinder assembly consequent on the distortion due to the applied pressure. Initially, these formulae will not involve any assumption as to the form of distortion; later, however, the results of introducing certain simplifying assumptions will be examined. Unless otherwise stated, it is assumed only that the piston and cylinder are initially straight and coaxial, that there is circular symmetry in all planes perpendicular to the axis, and that the pressure transmitting fluid in the interspace flows in accordance with the normal laws of viscosity.

The essential features of the system are shown diagrammatically in Fig. 1. The upward force due to the fluid pressure  $P$  applied to the base of the piston, corrected for the forces due to the pressure and movement of the fluid in the gap between the piston and cylinder, is balanced by the total downward force due to the load,  $W$ . We denote by  $r$  and  $R$  the radii of the undistorted piston and cylinder respectively,  $u(x)$  and  $U(x)$  the increases in these radii for a total applied pressure  $P$ ,  $p(x)$  the pressure in the interspace, and  $2h(x)$  the radial separation, at the axial distance

$x$  measured from the lower end of the piston,  $l$  the total length of engagement,  $A_p$  the effective area of the system at the applied pressure  $P$ , and write  $R - r = 2H$ , where all of  $H$ ,  $h$ ,  $u$  and  $U$  are very small compared with  $r$ .  $P$  and  $p$  are always to be interpreted as the amount by which the actual pressure in the system exceeds the ambient pressure — normally atmospheric — to which the balance is exposed, and the effective area as a factor of dimensions  $L^2$  which, when multiplied into the total applied pressure, gives the total downward force provided by the load which

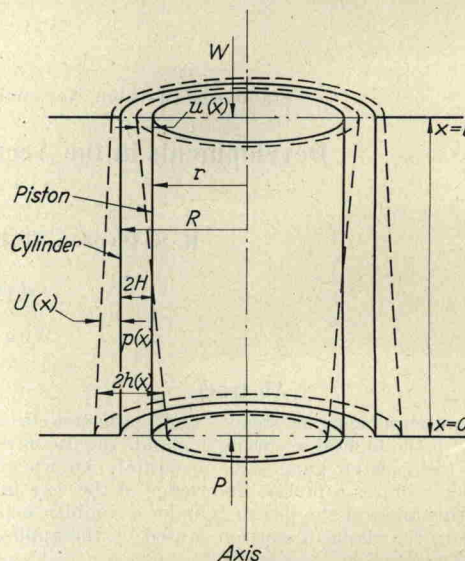


Fig. 1. Diagrammatic sketch of piston-cylinder assembly (clearance shown greatly exaggerated). — Undistorted boundaries of piston and cylinder, --- Distorted boundaries of piston and cylinder

is required to maintain the piston in equilibrium. For small applied pressures when distortion is negligible, we have from elementary considerations,

$$A_0 = \pi r^2 (1 + 2H/r) \quad (2.1)$$

neglecting second and higher-order terms in  $2H/r$ , where  $A_0$  is the effective area at zero pressure.

To obtain the more general formulae when distortion is present we note that the fluid forces acting on the piston have the following components:

a) upward force due to applied pressure on base of piston

$$P\pi r^2 [1 + 2u(0)/r];$$

b) upward force due to fluid friction on flanks of piston

$$2\pi r \int_0^l \left( -h \frac{dp}{dx} \right) dx,$$

$$= 2\pi r \int_0^l \left[ -\frac{d(ph)}{dx} + \frac{p}{2} \left( \frac{dU}{dx} - \frac{du}{dx} \right) \right] dx;$$

c) upward force due to vertical component of applied pressure on flanks of piston

$$2\pi r \int_0^l p \frac{du}{dx} \cdot dx.$$

Thus the total upward force acting on the piston is

$$P\pi r^2 [1 + 2u(0)/r] + 2\pi r \int_0^l \left[ -\frac{d(ph)}{dx} + \frac{p}{2} \left( \frac{dU}{du} + \frac{du}{dx} \right) \right] dx,$$

\* 1 bar =  $10^6$  dyn/cm<sup>2</sup> =  $10^5$  N/m<sup>2</sup>.