

(such as talc and graphite), the complicated boundary conditions arising from shearing resistance at the outer diameter and the influence of loading history. However, if the shearing resistance at the outer boundary is ignored for the present (it is considered separately below), a rough estimate can be made in the case in which the final pressure is approached from below.

Consider the idealized situation of a sample region of negligible shear strength surrounded by concentric cylindrical sleeves of graphite and another medium such as talc. Since the strengths of graphite and talc may be comparable, we assume them to be equal, as a first approximation. Further, we assume that, in the final pressure increment, yielding occurs throughout the pressure cell but that changes in volume and strength of the media during this increment are negligible. Then we have a relatively simple model in which the stress distribution can be calculated with the aid of the theory of plasticity. For a variety of yield and boundary conditions, this can be expected to lead to a nominal pressure correction that is proportional to the strength of the media, that is,

$$p = p_n - C\sigma_0$$

where

- p pressure in sample region,
- p_n nominal pressure applied to pressure cell (neglecting piston-cylinder and cylinder-medium friction),
- σ_0 stress difference that the medium supports at the appropriate pressure in the tests of the described above (c.f. uniaxial yield stress in plasticity theory),
- C a constant depending on the geometry of the pressure cell and on details of the yield criterion and boundary conditions.

If the axial stress at all points outside the sample region is assumed to exceed the pressure in the sample region by an amount σ_0 , C will have the value $1 - a^2/b^2$ where $2a$ is the diameter of the sample region and $2b$ the inside diameter of the pressure vessel. A more detailed calculation (Appendix), assuming a rigid pressure vessel and von Mises yield criterion for the media, gives an expression for C which is a more complicated function of a/b ; this is plotted in Fig. 12, from which it is seen that C is nearly unity for the range of values of a/b likely to be important in practice. It is also shown in the Appendix that allowing for the elastic distortion of the pressure vessel would still give the same form for C as that plotted in Fig. 12 but the relevant value of C would correspond to a larger value of a/b than that for the actual pressure cell; that is, in general, the value of C may be somewhat smaller than suggested by Fig. 12 (the more so for a steel vessel than for a carbide one) but it will probably still be not much less than unity for relevant values of a/b .

Thus, in a pressure vessel consisting of talc and graphite in which the average stress difference supported by these media is approximately 1 kb (that is, shear strength about 0.5 kb) and in which the sample region is not larger than about two-thirds of the diameter of the cell, the correction to the nominal pressure for the strength of the media alone should be approximately 1 kb. This figure may be expected to apply very roughly to many practical situations using talc at pressures of 20–30 kb and not to increase very much with pressure in this range.

If, contrary to the assumption above, the graphite has negligible strength (for example, if it is weakened by the pressure of water from decomposing talc), it

can be regarded as part of the sample region. Even then, the ratio a/b for the talc alone may still be in the range (Fig. 12) for which C is only slightly less than unity and so a similar correction would apply. On the other hand, for silver chloride and sodium chloride media, it follows from the present strength measurements that, as would be expected, the correction will be small compared with that for talc, although some correction may still be needed for the graphite furnace. In any case, the considerations in this section only apply when the final pressure is approached from below ("piston in"); the irreversibility is discussed in the comments below. Also, the compressibility of the medium has been ignored, although this is probably not serious at the level of approximation concerned here for "piston in" conditions.

(c) *Shearing between Pressure Medium and Cylinder Wall.* Since the coefficient of friction for sliding between the pressure medium and the wall of the pressure vessel is unlikely to be less than about 0.1, even with molybdenum disulphide lubrication, the shear stress parallel to the wall will generally tend to exceed the shear strength of the medium at pressures above 10–20 kb (and at much lower pressures in the case of silver chloride or sodium chloride). Therefore, we can usually take the shearing resistance at the wall to be equal to the shear strength of the medium, that is, about one-half of the stress difference σ_0 that the medium will support according to our tests, appropriately extrapolated. Thus the total shearing force required for shearing at the wall over a length l of the cylinder from the end of the piston to the level of the sample (usually l is about one-half of the total length of the pressure cell) is $2\pi bl \cdot \frac{1}{2}\sigma_0$. This corresponds to an increase in nominal pressure of $\frac{\pi bl \sigma_0}{\pi b^2} = \frac{l}{b} \sigma_0$, approximately equal to σ_0 in most practical cases. Thus, the nominal pressure correction for shearing at the cylinder wall should be approximately equal to the correction for stress gradient in the medium, namely, about 1 kb with talc at 20–30 kb pressure and not increasing much with pressure. If a thin layer of lead is used as a "lubricant", the shearing will occur in the lead, for which Bridgman (1935) gives a shear strength of 0.3 to 0.4 kb (that is, $\sigma_0 = 0.6$ to 0.8 kb) at pressures of 20–30 kb; the correction for shearing at the wall is then a little less than with talc alone but the difference is not appreciable.

(d) *Friction between Piston and Cylinder.* This will depend on the materials and clearances used in construction and on the use of anti-extrusion rings and lubricants. Our experience with 10 kb fluid medium apparatus, made from steel and using an anti-extrusion ring and O-ring packing lubricated with molybdenum disulphide grease, is that the friction is about $\frac{1}{2}$ to 1 percent (occasionally as high as 2 percent) of the load on the piston, provided that the clearances are large enough to avoid binding in the cylinder. This situation is rather similar to that in solid medium apparatus, suggesting a correction for piston friction of about 1 percent, although this could vary somewhat from apparatus to apparatus and it may not be strictly linear with pressure. Thus the correction to the nominal pressure for piston-cylinder friction would be 0.2 to 0.3 kb for 20 to 30 kb pressure.

Comments. These estimates are subject to considerable uncertainty and it may well be fortuitous that they add up to about 2.2 kb, roughly equal to the 10 percent correction suggested by Green *et al.* (1966), for pressures around 20 to 25 kb in talc. In particular, a gross approximation has been made in ignoring the inter-