J. Phys. E: Sci. Instrum., Vol. 16, 1983. Printed in Great Britain

Simple sensitive techniques for absolute and differential helium pycnometry

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Received 13 December 1982

Abstract. Techniques of absolute and differential helium pycnometry combining good sensitivity with simplicity of experimental equipment and procedure are described. These techniques are suitable for measuring the density of (or the adsorbability of He in) powdered or porous solids. Their application is illustrated here on pellets prepared by compaction of finely powdered ('colloidal') graphite.

1. Introduction

The development of sensitive techniques of helium pycnometry is of considerable importance. On one hand, He is a valuable pycnometric fluid for finely powdered or porous solids. Because of its small molecular size it can penetrate into narrow pores with a minimum of adsorption or excluded volume effects (e.g. Spencer 1967, de Boer and Steggerda 1958). On the other hand, if the 'true volume' V_{00} of the solid sample is known independently, then the apparent volume by He displacement, V_0, will yield (by difference) information about the adsorbability of He, or the presence of closed pores, etc (e.g. Maggs *et al* 1960, Dresel and Roberts 1953). Results of considerable physicochemical importance have been obtained from such measurements, including the first unambiguous observation of negative gaseous adsorption (Barrer and Petropoulos 1965).

The usual method of measurement is volumetric (although Springer *et al* (1969) have used a gravimetric technique). Its sensitivity depends on (i) the precision and accuracy with which the relevant volumes and gas pressures can be determined and (ii) the detailed design of the apparatus (particularly the possibility of minimising dead volume, as is discussed in more detail below). High sensitivity can of course, be achieved by the use of sufficiently sophisticated equipment (e.g. Constabaris *et al* 1959). However, for measurements at or near room temperature, techniques capable of high sensitivity but requiring only simple conventional equipment and experimental methods are possible. Here we present a simple design which minimises dead volume in the conventional 'absolute' volumetric method and then describe a differential pycnometric technique. Both methods are then applied to the pycnometry of graphite pellets.

2. Absolute He pycnometry

The absolute version of our apparatus essentially consists of two 10 mm precision bore tubes (A and B in figure 1), which form

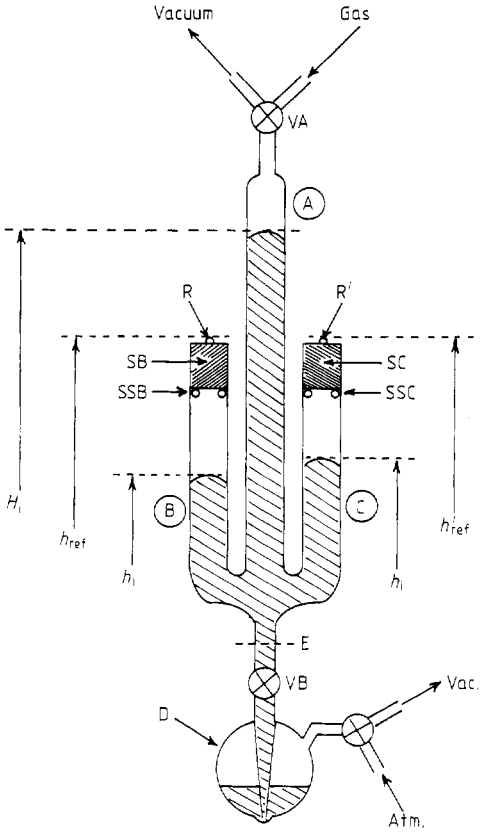

Figure 1. Apparatus for absolute (tubes A, B) and differential (tubes A, B, C) helium pycnometry: D, mercury reservoir; SB, test sample: SC, standard sample (for differential pycnometry); SSB, SSC, steel circular retaining springs; R, R′, fixed reference points.

the legs of a mercury manometer. A could be connected through stopcock VA to the vacuum or He gas supply, whereas B was closed with a flat top and contained the solid sample (SB). The latter was just under 10 mm in diameter and was held against the flat top of tube B by means of a thin circular spring (SSB). (To accommodate imperfectly consolidated or loose powder samples a thin glass filter paper may be inserted between sample and spring.)

Tube B was precalibrated with mercury by sealing it onto the manifold shown in figure 2. The tube and manifold were evacuated through stopcocks VC and VE with VD closed. Then mercury from reservoir F was allowed to rise just above VD. After further evacuation, VC and VE were closed and mercury was allowed to fill the manifold. Then through VC, mercury was raised to various positions h_i in tube B measured by means of a cathetometer. The position h_{ref} of a fixed point R on top of the tube was also determined. The corresponding weight losses of reservoir F gave the volumes of mercury having entered tube B. By subtraction from the volume of mercury required to fill tube B completely the void volume above the mercury column, V_i, corresponding to each h_i was determined. The uniformity of the cross-sectional area U of tube B was then checked by examining the linearity of the relation

$$V_i = (h_{ref} - h_i)U + a \qquad (1)$$

where the constant a indicates the position of zero void volume (which equals $h_{ref} + a/U$). The above method of calibration

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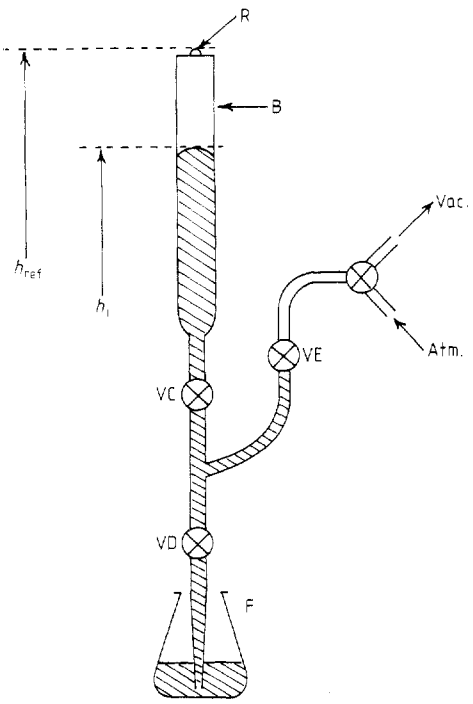

Figure 2. Apparatus for calibration of tube B(C): F, removable mercury reservoir.

eliminates the need for applying any significant meniscus correction to the subsequent volumetric measurements.

After calibration, tube B was cut away from the manifold, sample SB was inserted and the tube sealed in position in the apparatus of figure 1. After thorough outgassing with the mercury level at E, a suitable amount of He was introduced via VA into A and B. A certain portion of this gas was trapped in B and its volume varied by raising the mercury level to various positions h_i in B, while keeping A permanently evacuated. h_i and the corresponding mercury levels in A, H_i, were measured by means of the cathetometer. The new value of h_{ref} was determined likewise.

The volume V_0 of the sample (SB) follows from the relation

$$p_i(V_i - V_0) = K = \text{const.} \tag{2}$$

where $p_i = H_i - h_i$ and $V_i = (h_{ref} - h_i)U + a$ (cf equation (1)). If we consider the error ΔV_0 in the experimental value of V_0 caused by experimental errors Δp in p and ΔV in V, we find from equation (2)

$$\Delta V_0 = \Delta V + (V - V_0)\Delta p/p. \tag{3}$$

It is obvious that ΔV_0 is minimised if V can approach V_0 as closely as possible. This is achieved in our design by making the pelletised sample fit the closed end of tube B and allowing the mercury level to approach very close to the surface of the pellet. Thus, the only irreducible dead volume is that due to the porosity of the pellet and the curvature of the mercury meniscus. At the same time the presence of grease is avoided.

The sensitivity of this method of pycnometry is limited mainly by the precision and accuracy of the cathetometer, the reproducibility of the mercury meniscus and the constancy of the temperature.

3. Differential He pycnometry

A differential pycnometry technique was devised by adding a third limb to the manometer described above. This was a closed tube (C in figure 1), as closely similar to B as possible, containing a closely fitting metal cylinder impenetrable to He (SC) kept in position by the circular spring SSC. The volume of SC V_0', was accurately known and approximately equal to V_0. Tube C was precalibrated exactly like B and sealed in a position as nearly symmetrical to that of B as possible. This design ensured that the fixed reference points (R, R' in figure 1) and the mercury levels in B and C were always at about the same height. Thus the differences $\delta h_{ref} = h_{ref} - h'_{ref}$ and $\delta h_i = h_i - h'_i$ were within the range of a micrometer gauge and hence measurable with greater accuracy and precision than is usually possible with a cathetometer.

A relation analogous to equation (2) es to tube C, namely

$$p'_i(V'_i - V'_0) = K' = \text{const.} \tag{4}$$

Subtraction of equation (4) from (2) yields

$$p_i\delta V_i + (V'_i - V'_0)\delta p_i = p_i\delta V_0 + K - K' \tag{5}$$

where

$$\delta V_0 = V_0 - V'_0;\ V'_i = U'(h'_{ref} - h'_i) + a'$$

$$\delta p_i = H_i - h_i - (H_i - h'_i) = -\delta h_i$$

$$\delta V_i = U(h_{ref} - h_i) - U'(h'_{ref} - h'_i) + a - a'$$

which for $U = U'$ reduces to

$$\delta V_i = U(\delta h_{ref} - \delta h_i) + a - a'.$$

From equation (5) we find that the error $\Delta\delta V_0$ in δV_0 (and hence also in V_0) caused by experimental errors Δp, $\Delta V'$, $\Delta\delta p$ and $\Delta\delta V$ in p, V', δp and δV respectively is given by

$$\Delta\delta V_0 = \Delta\delta V + \delta p\Delta V'/p + (\delta V - \delta V_0)\Delta p/p + (V' - V'_0)\Delta\delta p/p$$

and since $\delta V/p$, $\delta V_0/p$ and $\delta p/p$ are small

$$\Delta\delta V_0 \cong \Delta V_0 \cong \Delta\delta V + (V' - V'_0)\Delta\delta p/p. \tag{6}$$

Comparison of equations (3) and (6) shows that the superiority of the differential technique over the absolute one depends on making $\Delta\delta V$, $\Delta\delta p$ smaller than ΔV, Δp respectively. This is made possible, in turn, by the aforementioned more accurate and precise measurement of differential displacements and by the automatic compensation of temperature variations afforded by the differential technique. Any tendency of He to be significantly absorbed by glass (cf Ash *et al* 1966) is also compensated for in the case of differential pycnometry.

4. Experimental

The techniques described above were applied to pellets prepared by compaction of colloidal graphite powder (Acheson DAG 621 dispersion powder of specific surface area 70 $m^2\,g^{-1}$ and ash content 0.29%). A 7 g powder sample (SB) was compacted in portions of *ca* 1 g at a time in a cylindrical die of diameter just under 10 mm to a porosity of *ca* 0.15. The resulting pellet was inserted in tube B, outgassed at temperatures up to 523 K (250 °C) for several days prior to the volumetric measurements; and its outgassed weight determined after their conclusion. The standard sample (SC) inserted in tube C was an aluminium alloy cylinder machined to the proper dimensions. Its volume V'_0 was accurately measured by weighing in water. The volumes of the retaining springs SSB and SSC were determined similarly. Helium gas was of 99.95% purity. Triple-distilled mercury was used for the calibration of tubes B and C. All measurements were carried out at room temperature by means of a cathetometer reading to 0.01 mm and a micrometer gauge (mounted on the same stand) reading to 0.001 mm. Care was exercised to raise the mercury level reproducibly and to preserve the same meniscus shape as far as possible in all pycnometric

and calibration measurements. Room temperature was usually between 296 and 297 K (23–24 °C). Its maximum variation for the whole series of measurements was ~2 K, but the change during a given run did not exceed ~0.5 K.

5. Results and discussion

The calibration plots of V_i against $(h_{ref}-h_i)$ for tubes B and C, shown in figure 3, exhibited satisfactory linearity (linear regression coefficients $r=0.99998_6$ and 0.99999_2 respectively), yielding $U=0.783_8$ cm^2, $U=784_4$ cm^2: $a=-0.151_0$ cm^3, $a'=-0.133_1$ cm^3.

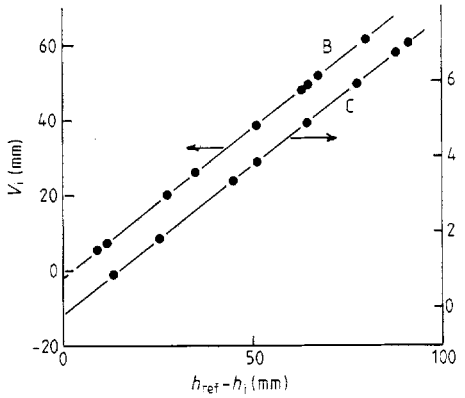

Figure 3. Calibration lines for tubes B and C (cf equation (1)).

The results reported in table 1 and figures 4 and 5 were obtained from three runs using the same quantity of He plus two more using different quantities of gas. Parallel cathetometer and micrometer gauge readings were taken. In this way both absolute and differential pycnometry techniques could be applied in each case and V_0 deduced from the slope of the appropriate linear regression based on equations (2) and (5) respectively (figures 4 and 5 respectively).

Table 1. Results for $V_0(V_0')$ in cm^3 obtained by absolute and differential He pycnometry.

Absolute		Differential	
V_0	V_0'	δV_0	V_0
3.118	3.091	0.026_6	3.122_3
3.121	3.092	0.027_0	3.122_7
3.110	3.083	0.027_4	3.123_1
3.134	3.106	0.029_4	3.125_1
3.132	3.106	0.027_7	3.123_4
Mean			Mean
3.123	3.095_5		3.123
Std error			Std error
0.004_5	0.004_5		0.005

A valuable check of the measurements was provided by analysis of the data on the standard sample, on the basis of equation (4) (see figure 4). The mean value of V_0' so determined (table 1) agreed very closely with $V_0'=3.095_7$ m^3 obtained by weighing in water. This result indicates, incidentally, no significant sorption of He by the glass of our apparatus. On the other hand, the mean values of V_0 obtained by the absolute and differential techniques also show excellent agreement (table 1).

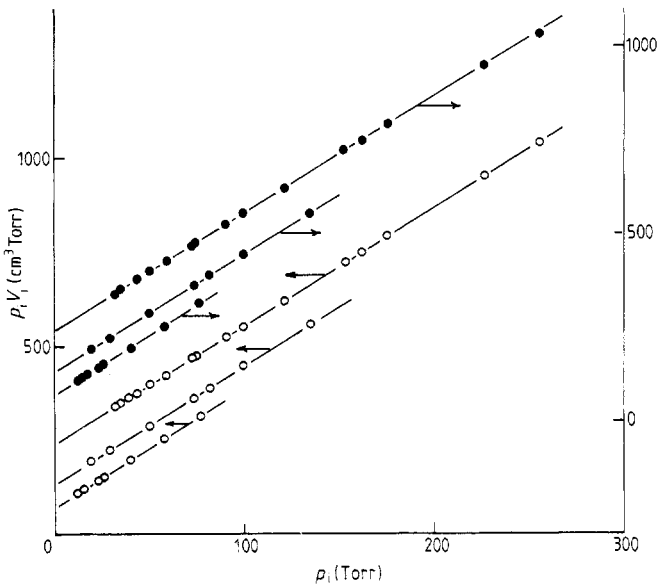

Figure 4. Linear plots of the results of absolute helium pycnometry of graphite (○) and standard (●) samples plotted according to equation (2).

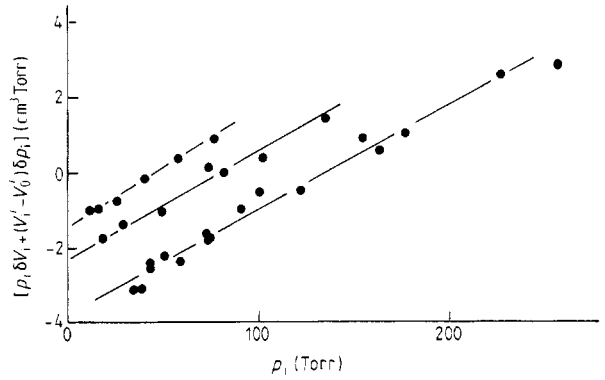

Figure 5. Linear plots of the results of differential helium pycnometry of the graphite sample according to equation (5).

The superiority of the differential pycnometric results lies in the much lower variability of the V_0 values for the individual runs. The absolute pycnometric results can, no doubt, be improved markedly (at some expense in the simplicity of the apparatus) by precise temperature control. Similarly, the differential technique would gain in accuracy by repeating the measurements with test and standard sample interchanged.

The above results yield a density for graphite of 2.206 g cm^{-3}, which is considerably lower than the value quoted for pure natural graphite (2.251 g cm^{-3}) or the x-ray density (2.266 g cm^{-3}). It appears, therefore, likely that there is appreciable void volume inaccessible to He in the pellet examined.

6. Conclusion

The results quoted above demonstrate that helium pycnometry of powdered and porous solids in the neighbourhood of room temperature can be performed with good sensitivity using only the simplest experimental equipment and methods. The success of the differential pycnometric technique introduced here is

paticularly noteworthy, because the same approach should be potentially useful also in the case of more sophisticated apparatus (e.g. by exploiting the high sensitivity of capacitative or similar differential pressure gauges).

Acknowledgments

This work was sponsored by the Hellenic Atomic Energy Commission. A scholarship for CS was provided by the National Research Foundation. The support and interest of Professor Th Yannakopoulos is also gratefully acknowledged.

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