FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

TECHNICAL MEMORANDUM NO. 16 OF 1967

A MICRO VOLUMETRIC GAS ADSORPTION APPARATUS

By:

P.G. SEVENSTER

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In studies concerning the weathering of sandstones, shales and minerals associated with coal it is necessary to investigate the affinity that these substances have for atmospheric oxygen and water vapour.

Although these materials do not consume large amounts of oxygen or water vapour it is possible to detect significant weathering tendencies by means of their behaviour towards atmospheric gases and vapours.

For example in the case of some shales it is well known that weathering is accelerated by loss or gain of water vapour. It is also common knowledge that marcasite and pyrites exhibit different chemical properties although they have identical chemical compositions. Furthermore, these iron disulphide compounds are more susceptible to oxidation in a fine state than when they occur as large crystals or nodules.

The oxygen adsorption characteristics of these materials are best studied by means of a gas-volumetric system. The quantities of gas involved may be so small that a conventional adsorption apparatus could not be used.

Attention was therefore given to the development of a more sensitive technique for studying adsorption phenomena. The outcome of this development work was an apparatus which can measure quantities of gas as small as one thousandth of a cubic centimeter with fair accuracy.

The apparatus is especially suitable for surface area measurements which is also of importance in the study of mineral weathering.

THE PRINCIPLE:

The principle of the technique is to balance the pressure in two identical systems; the one system contains helium which is not adsorbed, and the other contains a gas which is adsorbed by the adsorbent.

The ...../

The pressure balance between the two systems is accomplished by changing the volume of one system by raising or lowering the mercury contained in a burette until zero pressure difference is attained as indicated by a differential manometer.

The amount of volume change required to balance the pressure is equal to the amount of gas adsorbed at the prevailing pressure.

THE APPARATUS:

The apparatus consists essentially of two conventional gas-volumetric systems of identical volume coupled to each other by means of a differential manometer.

The adsorption bulbs (A in Figure 1(a)) should be of identical volumes especially those parts which are subjected to a temperature different from that of room temperature. The volumes are checked by filling with mercury and weighing. These bulbs are fitted with ground glass joints for fixing to the volumetric systems.

The horizontal arms of the systems are constructed of 2 mm bore tubing to minimize the free space.

The manometer M_3 is used to measure the pressure in the system with respect to vacuum. The manometer M_2 is a differential manometer by means of which difference in pressure between the two systems is observed.

The movement of the mercury in the wide tubes (2 cm.) of the manometer is magnified by coupling a capillary loop (2 mm.) partly filled with air to the wide tubes by means of a four way stop-cock (S_3) (See Figure 1(b)).

The air column can be isolated (by turning the plug into position 2, indicated in sketch by $\longrightarrow$ 2) while the apparatus is being evacuated and rough pressure adjustments made.

When the plug is turned into position (1), (indicated by $\uparrow$ 1) the two legs of the manometer are connected to each other through the loop and the air column.

This arrangement permits the adjustment of the pressure difference to within 10^{-3} mm. Hg. The magnification is determined by the ratio of the areas of the tubes which is 1:100 for 2 cm and 2 mm tubes. Therefore, if a difference of 0.1 mm can be observed in the height of the capillary columns -

the ...../

the actual pressure difference will be $\frac{0.1}{100} = 10^{-3}$ mm Hg.

Since this manometer is used only as a null indicator the wide limbs need not be longer than about 5 to 10 cm. On the other hand, the length of the capillary loop should be sufficient to allow for the considerable magnification of differences in mercury heights that take place in it. A total length of about 20 cm has been found satisfactory. The wide tubes of the manometer are also used for calibration purposes and should be constructed from constant bore tubing.

Pressure difference adjustments are made by lowering the mercury in B, which is a capillary tube, the size of which can be selected for a particular adsorption range.

The manometer M_1 is used for initial metering of the volumes of the gases admitted to the systems.

If B and M_3 are constructed of the same diameter tubing and are of the same length, changes in the atmospheric temperature will be automatically compensated for by expansion or contraction of the mercury in these tubes.

CALIBRATION:

It is necessary to have identical volumes in the two systems between the points indicated by arrows.

If the adsorption bulbs (A) have identical volumes, it is a fairly simple operation to ensure that the total volumes are the same by adjusting the mercury heights in B and M_3.

To check the volumes the procedure is as follows:-

The empty adsorption bulbs are fixed to the system and evacuated after the mercury in the manometer M_1, M_2 and M_3 has been lowered.

After evacuation the mercury is raised into M_3 to a position marked by the arrow. In M_2 the mercury is raised to a position fairly low in the limbs but high enough to cover irregularities in the constant bore limbs, caused by glass-blowing when the horizontal limb was fixed. The mercury and air column in the capillary loop was previously admitted and are isolated during the initial operation. In B it is admitted to the position indicated by the arrow.

Mercury is admitted into M_1 to about 10 cm above the stop-cock (S_6).

Helium ..../

Helium and argon (or oxygen in the case of oxidation studies) are now carefully admitted to M_1 through S_1 and S_2 to roughly equal pressure.

S_2 is opened and helium admitted to the space to be calibrated. Care must be taken that mercury in M_2 is not pushed over. S_2 is then closed again. S_4 is now opened to allow argon into its section until zero pressure is indicated by M_2. This is accomplished by closing S_6 and shifting the mercury up or down as required. S_1 is then closed.

The air column in M_2 is now connected (by means of S_3) and zero pressure difference obtained by shifting the mercury in either B or M_3.

The volumes of the helium and argon systems are now decreased by identical volumes by raising the mercury in the constant bore tubing of M_2. S_4 in M_3 is closed during this operation to eliminate continual adjustment to a fixed setting of this mercury column.

If the two systems have identical volumes no pressure change on M_2 will be observed when the mercury is raised in it. If the volumes are unequal a pressure difference will be indicated. By repeated adjustment of the mercury in M_3 or B and rechecking, the volumes of the two systems can be made the same. It must be noted that after each adjustment in B and M_3 the initial volumes of gas admitted must also be corrected by adjustment in M_1.

After final checking, the positions of the mercury in M_3 and B are accurately marked. The position of the mercury in M_2 is not critical since the diameters are equal. It is, however, advantageous to have the mercury as high as possible to minimise the free space.

PROCEDURE FOR SURFACE AREA MEASUREMENTS:

The adsorption bulbs are filled with equal amounts of sample and fitted to the system and evacuated.

Helium and argon are admitted (as already described) to the desired pressure (on M_3) and the pressure difference (on M_2) adjusted to zero (by M_1).

Refrigerant is then placed around A and B, and the pressure adjusted to zero on M_2. At equilibrium, readings are taken of pressure on M_3 and volume adsorbed on B.

To ...../

To make measurements at higher pressures the refrigerant is removed and the mercury in B brought back to the zero reference mark. Gas from M_1 is then admitted at a higher pressure and the procedure repeated.

PROCEDURE FOR OTHER ADSORPTION STUDIES:

The same procedure is followed as before, except that the argon system is filled with the gas to be investigated.

SOME CALCULATIONS TO DEMONSTRATE THE CAPABILITIES OF THE TECHNIQUE.

The response of the manometer to pressure change and the minimum volume change that can be effected by shifting the mercury in the burette B determine the sensitivity of the method.

The response of the manometer (M_2) is determined by (1) the sensitivity, (2) the free space in the system and (3) the prevailing pressure in the system.

The sensitivity of the manometer is 10^{-2} mm Hg if it is assumed that the difference in mercury levels in the capillary loop can be accurately read to 1 mm.

The free space in the system is about 2.5cc, including the space in an adsorption bulb large enough to hold 10 gm of sample.

The volume change effected by 1 mm shift of the mercury in B (2 mm diam.) is equal to .003 cc.

Suppose now, measurements are to be made at 5 cm Hg pressure and that the room temperature is 25°C, an increase in volume from 2.5 to 2.503 cc causes a drop in pressure,

$$P_2 = \frac{2.5 \times 5}{2.503} = 4.990$$

$$\therefore \Delta P = 5.0 - 4.990 = 0.01 \text{ cm.}$$

This pressure difference is magnified in the capillary loop of the manometer to .01 X 100 = 1 cm. which is easily detected. The equivalent volume of gas, at N.T.P. will be

$$.003 \times 5 \times \frac{273}{76 \times 298} = 2.0 \times 10^{-4} \text{cc at N.T.P.}$$

To summarize, a shift of 1 mm on B (2 mm.diam.) is equivalent to a volume change of .003 cc and causes a pressure change of 0.01 cm. Hg magnified to 1cm. at a pressure of 5 cm. Hg in a free space of 2.5 cc, and finally, the amount of gas involved at N.T.P. is about 2.0×10^{-4}cc.

Comparing this quantity of gas with a V_m (the monolayer capacity) of say 10 gm. of sample of 10 cm^2/gm surface area it

appears ...../

appears that this technique is capable of measuring quantities of gas far smaller than would be adsorbed by this sample (to complete a monolayer) viz.:

V_m(for argon). = $(\frac{1}{3.87})$cc (N.T.P.) per gm.
= 2.5×10^{-3}cc (N.T.P.) per 10gm.

EXAMPLE:

The argon-isotherm for a one gram sandstone sample was determined up to $P/P_o = 0.4$ and the surface area calculated.

FACTORS:

L= distance of shift of mercury in B (4mm dia.)

V= volume change = πr^2 L
= $3.14 \times (.2)^2 \times L$
= $0.126 \times L$

V_a= volume adsorbed at N.T.P. = $\frac{273}{76 \times 298} \times 126$ LP
= 1.54×10^{-3} LP cc.

P (cm)	L (cm)	$V_a$cc	P/P_o
9.3	15.4	0.22	0.1
13.1	12.1	0.25	0.15
17.8	9.9	0.27	0.2
26.5	8.3	0.34	0.3
34.0	7.65	0.40	0.38

B.E.T. Calculation.[Θ]

$S = \frac{1.8}{.5} = 3.6$; $1 = 0.2$; $V_m = \frac{1}{3.8}$

$S_o = \frac{3.872}{3.8}$ * $= 1.02$ $m^2/gm.$

* Factor to convert V_m to S_o

It must be noted that corrections for thermal transpiration and the imperfections in the gas used as adsorbate are required when making measurements of the monolayer capacity of samples with small surface areas.

Θ Brunauer, Emmett, P.H., Teller, E., J. Am. Chem. Soc. 60, 309, 1938.

ADVANTAGES OF THE TECHNIQUE:

The main advantages of the technique are the following:

(1) A free space calibration is not required for each sample to be investigated.

(2) Initial adjustment of volumes are easily and accurately accomplished, except the volumes of the adsorption bulbs which require some skill.

The ...../

(3) The volume of the measuring system is constant and can be reduced to a minimum with resulting high sensitivity at low pressures.

(4) The apparatus compensates automatically for changes in room temperature.

(5) Only a few simple calculations are involved.

(6) The pressure change caused by adsorption is measured on a sensitive null-point device.

THE DISADVANTAGES ARE::

(1) Two identical samples are required.

(2) The construction of identical adsorption bulbs is difficult.

(3) After each equilibrium point has been determined the refrigerant must be removed to allow the adsorbent to attain room temperature before adjustments to higher gas pressures can be made.

(4) Desorption runs can only be made to the extent permitted by the volume increase in the system effected by the lowering of mercury in the constant bore tubing of the manometer M_2. Loss of sensitivity is involved in this procedure because of increase in the free space.

PRETORIA
3rd July, 1967.

P.G. SEVENSTER.
Principal Research Officer.

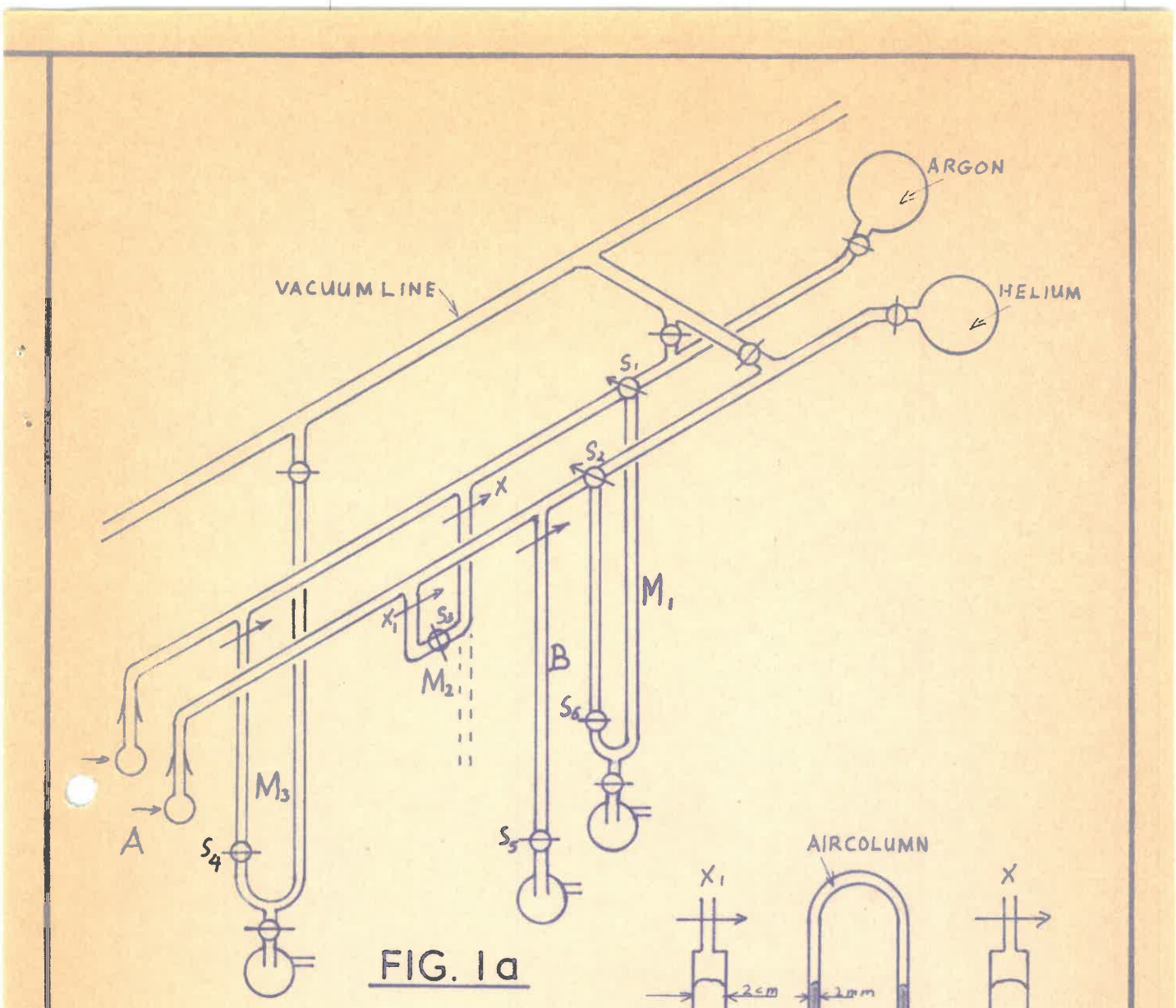
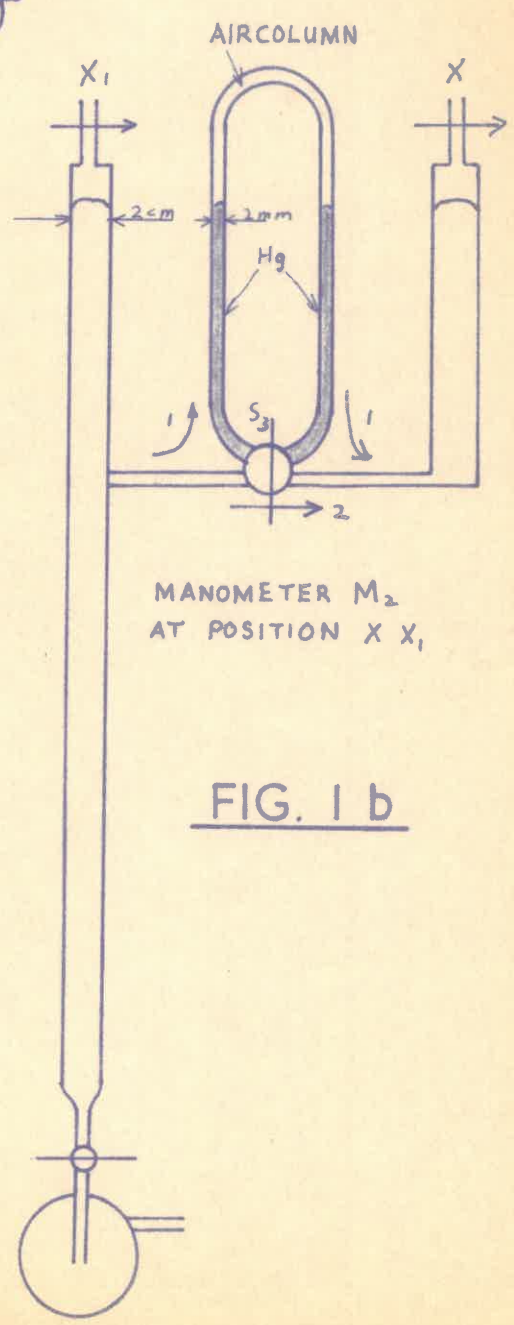


FIG. 1a

MICRO VOLUMETRIC GAS ADSORPTION App.



MANOMETER M_2
AT POSITION X X_1

FIG. 1b