

## LETTERS TO THE EDITOR

### CALIBRATION OF SAMPLE TUBE DEAD SPACE IN ADSORPTION EXPERIMENTS WITHOUT USING HELIUM

IN the determination of the surface area of solids by volumetric gas adsorption methods, one of the necessary steps is the calibration of the sample tube dead space (STD). The general practice is to use helium for this purpose. An alternative method, using nitrogen or any other gas in the place of helium, has been worked out by Loebenstein.<sup>1</sup> In this method, the geometric volume of the STD is determined at two different temperatures at which the gas is not adsorbed. The methods described in this paper are, in principle, similar to Loebenstein's method, but lead to a higher accuracy.

Figure 1 shows a part of a standard volumetric adsorption apparatus in which the volumes B and C form the sample tube dead space. A is the manometric dead space which is constant for the apparatus and can easily be

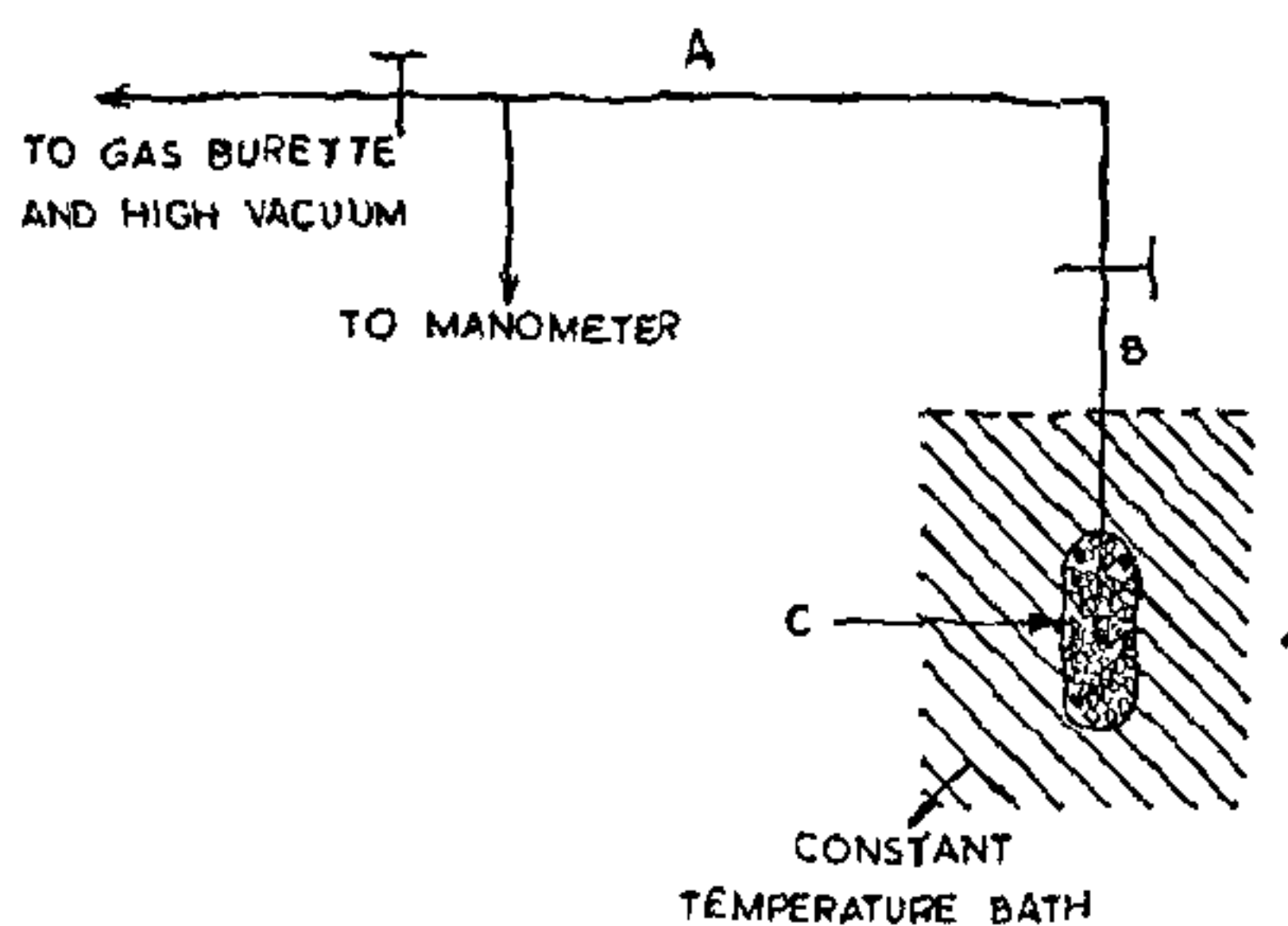


FIG. 1. Schematic of an adsorption apparatus.

determined by the expansion of a known amount of a gas. C is immersed in a constant temperature bath during an adsorption run and B is exposed to room temperature. The geometric volume of B and C can be determined by one of the following methods.

(1) Let the absolute volumes of the dead spaces A, B and C be  $V_A$ ,  $V_B$  and  $V_C$  respectively. Let the volumes of gas present in these dead spaces at standard temperature and pressure be  $V_{A(NTP)}$ ,  $V_{B(NTP)}$  and  $V_{C(NTP)}$  respectively. A known quantity ( $V_{(NTP)}$ ) of a gas, say nitrogen, is taken in the dead spaces

A, B and C. C is immersed successively in baths maintained at different temperatures and the corresponding pressures are noted. Then,

$$\frac{P_0 \cdot V_{(NTP)}}{T_0} = \frac{P(V_A + V_B)}{T_r} + \frac{P \cdot V_C}{T} \quad (1)$$

where P is the pressure in the system at the bath temperature T,  $T_r$  is the room temperature,  $P_0$  and  $T_0$  are the standard pressure and temperature. On rearranging Eqn. (1) we get,

$$\frac{1}{P} = \frac{(V_A + V_B) T_0}{V_{(NTP)} T_r P_0} + \frac{T_0 \cdot V_C}{P_0 V_{(NTP)}} \cdot \frac{1}{T} \quad (2)$$

$V_{(NTP)}$  being constant, a plot of  $1/P$  against  $1/T$  will be a straight line. From the slope and the intercept,  $V_C$  and  $(V_A + V_B)$  are calculated.

This method requires that the room temperature  $T_r$  is constant. If there are fluctuations in  $T_r$ , the accuracy of the method will be affected in two ways: (i) the value of  $(V_A + V_B)$  obtained from the intercept will be erroneous and (ii) the term corresponding to the intercept in Eqn. (2) will not be constant, thus affecting the linearity of the straight line.

(2) To minimise the errors arising out of fluctuations in  $T_r$ , a different approach may be adopted. Let  $V_{BC}$  be the volume of the STD, and the volume of the gas occupying the dead space be  $V_{BC(NTP)}$ . Now, at every bath temperature,  $V_{BC(NTP)}$  can be calculated, since,

$$V_{BC(NTP)} = V_{(NTP)} - V_{A(NTP)} \quad (3)$$

By recording  $T_r$ ,  $V_{A(NTP)}$  and hence  $V_{BC(NTP)}$  can be calculated accurately.

$$\frac{P_0 V_{BC(NTP)}}{T_0} = \frac{P \cdot V_B}{T_r} + \frac{P V_C}{T} \quad (4)$$

Hence,

$$\frac{V_{BC(NTP)}}{P} = \frac{V_B T_0}{T_r P_0} + \frac{V_C T_0}{P_0} \cdot \frac{1}{T} \quad (5)$$

A plot of L.H.S. of Eqn. (5) against  $1/T$  will be a straight line, whose intercept and slope will give the values of  $V_B$  and  $V_C$  respectively.  $V_B$  being small, any variation in the term  $\frac{V_B T_0}{T_r P_0}$  of Eqn. (5) arising out of the fluctuations in  $T_r$ , would be too small to affect the linearity of the plot.

Procedure 2 is applicable only to a constant volume adsorption system, but procedure 1 can be adapted for a system with an open limb

manometer. For this purpose, the total pressure in the dead space is held constant at every temperature by suitably varying  $V_{(NTP)}$ . A plot of  $V_{(NTP)}$  against  $1/T$  will be a straight line. From the slope and intercept,  $V_c$  and  $(V_A + V_B)$  are calculated.

$V_B$  and  $V_C$  are the volumes of B and C. The quantity of gas occupying these dead spaces is calculated by converting  $V_B$  and  $V_C$  to NTP by employing the temperature and pressure at which the adsorption experiment is conducted. If the temperatures at which the adsorption and dead space determinations are carried out, are very much different from each other, a correction may be applied to account for the contraction of glass. This correction, however, is small and is, normally, about 0.1% for every 100° temperature difference.<sup>1</sup>

In order to check the reliability of the above methods, the dead space obtained from procedure 2 using nitrogen was compared with that obtained by the conventional method using helium at  $-184^\circ\text{C}$ . The temperatures used for the determination of the absolute dead space with nitrogen were  $0^\circ$ ,  $31.2^\circ$ ,  $61.0^\circ$ ,  $82.0^\circ$  and  $110^\circ\text{C}$ . Liquid paraffin heated in a well-regulated electrical furnace was used as the bath material. The volume (NTP) of the gas present in the dead space obtained by the two methods are plotted as a function of pressure in Fig. 2. It is seen from the figure that the agreement between the present method and that using helium is excellent.

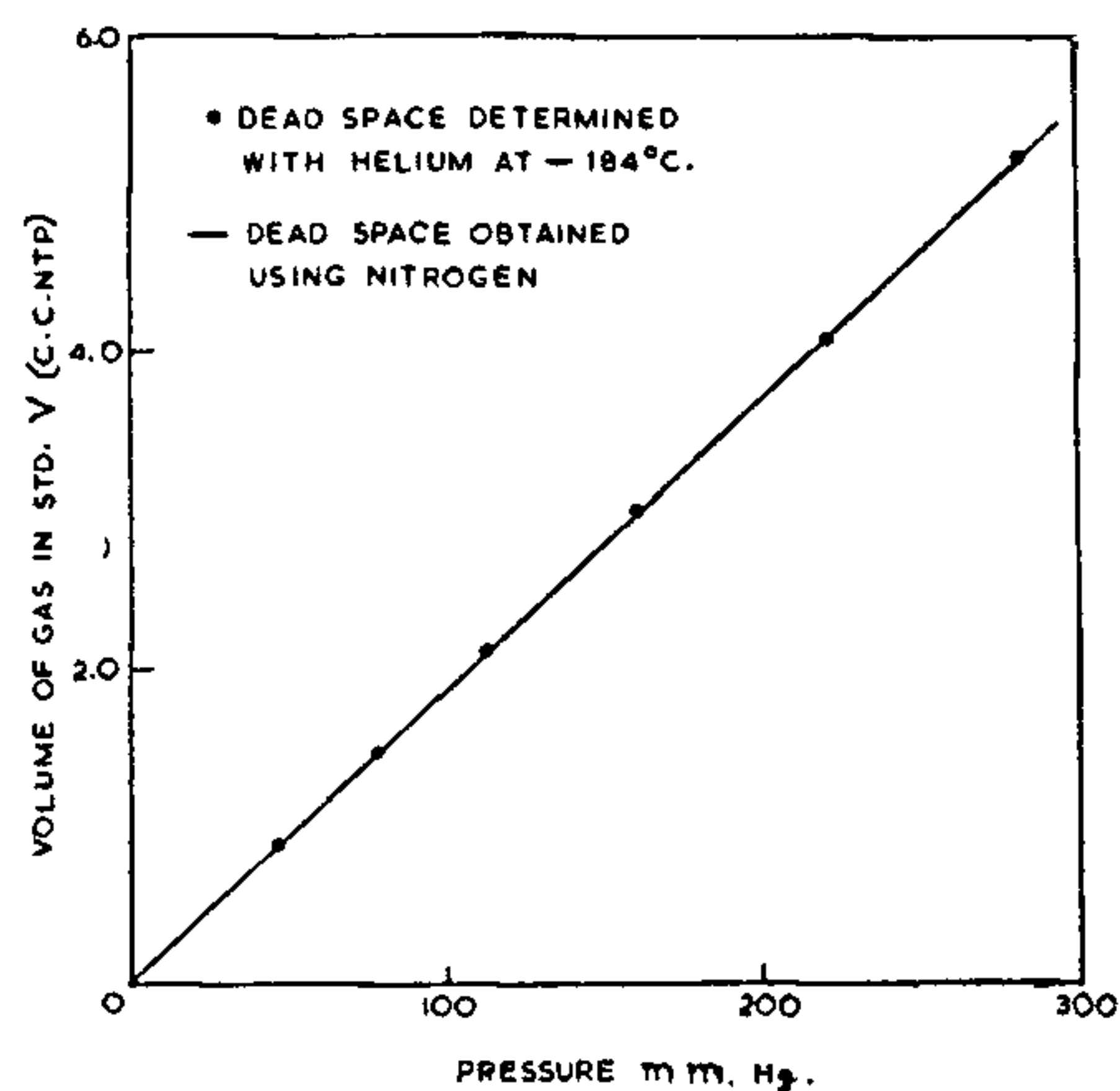


FIG. 2. A comparison of the calibration of sample tube dead space by the procedure 2 and by employing helium at  $-184^\circ\text{C}$ .

In the method described by Loebenstein,<sup>1</sup> theoretically, two experimental points are sufficient to calculate the absolute volumes of the dead spaces. However, to avoid experimental errors, an average of several determinations would be needed. In the present method, it is simpler to get a set of pressure readings by varying the bath temperature and the straight line graph gives the best average value of the dead space. A set of constant temperature baths can also be obtained by using salts having well-defined transition temperatures. It is important to employ only such temperatures at which the gas is not adsorbed. Nitrogen can be used in a temperature range of  $0-100^\circ\text{C}$ . even in the case of samples with large surface areas such as silica gel, metal oxides, etc. On metal surfaces, inert gases such as argon should be used.

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### VARIABLE ORDERS IN THE BROMINATION OF *p*-NITROPHENOL

BROMINATION of aromatic substrates by molecular bromine in organic solvents often exhibits complex kinetics as evidenced by the variable orders in bromine. In acetic acid medium, the reaction is generally second order in bromine and first order in substrate at high concentrations of bromine. At low concentrations, the orders are one in each. For the overall third order process, the mechanism involves the electrophilic attack of a molecule of bromine on a 1:1 complex of bromine and the substrate in the rate-determining step.<sup>1</sup> In the second order process, the complex undergoes electrophilic attack by the molecules of solvent due to the low concentration of bromine. This kinetic interpretation has been found to be valid for substrates like anisole<sup>2</sup> and *p*-bromophenol.<sup>3</sup> It was considered interesting to see whether the same mechanism would still hold good for a comparatively less reactive substrate like *p*-nitrophenol where the susceptibility to electrophilic attack is less.

The kinetics of the bromination of *p*-nitrophenol was followed by determining the