

AN INVESTIGATION OF THE RELIABILITY OF ADSORPTION MEASUREMENTS IN THE ULTRA LOW PRESSURE REGION

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INTRODUCTION

The data of physical adsorption have been used for many years as the basis for methods to characterize the surface area and porosity of adsorbents. Typically, adsorption isotherm data are acquired over a range of pressure from about 1 to about 760 torr. The measurements are commonly made with nitrogen as the adsorptive at its normal boiling temperature near 77K. The traditional experimental range is therefore about 0.001 to 1.0 when expressed as relative pressure.

This pressure range has been sufficient for the determination of surface area by the BET or Langmuir methods and for the characterization of mesopore size distributions by methods based on the Kelvin equation, such as the BJH method. However, it is now recognized that the characterization of microporous materials such as active carbons and zeolites by means of physical adsorption data requires that measurements be made at much lower relative pressures. It has been calculated by density functional theory and by molecular simulation[1,2] that pores of near-atomic dimensions (ca. 3.5 - 4.0 Å) fill with adsorbate at a relative pressure below 1×10^{-7} (< 0.1 mtorr in the case of nitrogen adsorption at 77K).

The extension of the range of adsorption measurements by four decades to the ultra low pressure region presents a new set of experimental difficulties and considerations that require attention or solution. Among these considerations are: rate of transport of gas through restrictions, rate of heat loss from the sample under vacuum, thermal transpiration (the spontaneous flow of gas from a cold to a warm region), and the selection of pressure measurement transducers.

BACKGROUND

Fig. 1 shows a schematic diagram of the essential elements of an adsorption apparatus. The type shown is unimanometric, in that the quantity of gas admitted to the system is measured by the same manometer as that used to determine the equilibrium pressure.

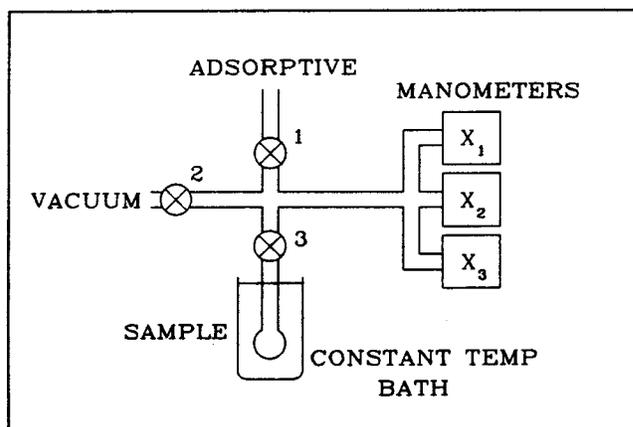


Figure 1. Schematic diagram of an adsorption apparatus.

We will refer to the part of the system connecting valves 1, 2 and 3 with the pressure transducers as the system manifold.

The manifold volume is commonly calibrated by allowing a measured pressure of helium to expand through valve 3 into a known volume attached in place of the sample cell and applying the ideal gas law. This obviously requires knowing the temperature of the manifold and of the calibration volume. The manifold now becomes a permanent reference volume for measuring the quantity of adsorptive admitted to the system in terms of the manifold pressure, p :

$$n_m = F_m * p \quad (1)$$

where n_m is the moles of adsorptive in the manifold, and F_m is a factor equal to V_m/RT_m .

Similarly, a "dead space" factor is determined by expanding a known pressure p of helium from the manifold into an evacuated sample cell through valve 3 with the constant temperature bath in place. If the final pressure is p_e , then it follows that

$$F_d = F_m * p/p_e \quad (2)$$

hence the quantity of adsorptive in the system when valve 3 is open is given by

$$n_d = F_d * p_e \quad (3)$$

Starting with a well-degassed sample and all valves closed, an adsorption isotherm is measured by admitting a "dose" of adsorptive to the manifold to an increment of pressure Δp , followed by opening valve 3. When equilibrium is reached, the pressure of the first isotherm point is recorded. The moles adsorbed is given by

$$n_{ads} = F_m * \Delta p - F_d * p_e \quad (4)$$

In general, since the moles admitted to the system are cumulative, we have

$$n_{ads(i)} = \sum_i F_m * \Delta p_i - F_d * p_{e(i)} \quad (5)$$

DESIGN CONSIDERATIONS

The first major consideration is that the system allow rapid evacuation to low pressure. For the investigation of microporosity, the vacuum pump should yield pressures below about 1×10^{-5} torr. The manifold passages should be short, and as large in diameter as possible commensurate with system volume considerations.

Once evacuated, the system should show a suitably low outgassing rate. This is a function of the materials of construction and the cleanliness of the system. If the outgassed species is not adsorbed, e.g. helium residue from freespace measurement, then the measured equilibrium pressures will be too high; if the contaminant is adsorbed, then the sample surface will also be contaminated, with variable effects.

The manometers used must display excellent linearity and stability and have low noise. Good manometers can be used at a resolution of 50 ppm of full scale. To cover the desired ultra low range requires three transducers, usually 1, 10 and 1000 torr as full scale. Allowing for resolution, one can therefore expect to measure a relative pressure (N_2 at 77K) of 1×10^{-6} as $760 \pm 50 \times 10^{-6}$ torr, or an uncertainty of around 6%. The error in quantity adsorbed is very much less, however, as the moles admitted to the system are measured at much higher pressure and the first term on the right of equation (5) predominates[3].

A major effect in the ultra low pressure region is due to the fact that a gas tends to pass from the low

temperature to the warmer region, and a steady state is reached when the pressure difference between the two regions is sufficient to balance this thermal effusion or transpiration [4]. The needed correction can be calculated by the equations of Miller [5]. The true equilibrium pressure is about 0.65 of the measured pressure at 5 mtorr, for nitrogen at 77K, and the ratio is about 0.51 for all pressures below about 3 mtorr. The correction is negligible at pressures above 100 mtorr. The data in Fig. 2 are illustrative.

CONCLUSIONS

The data of Fig. 2 were obtained on a commercial instrument with a sample of graphite, Sterling FT-G(2700)(aka P-33) known to be energetically uniform for adsorption and known to display linear, Henry's Law behavior (Ref. 3, p. 231). Data of this quality requires good high vacuum, a clean system, transducers with excellent zero stability and linearity, and accurate correction for thermal transpiration. Any system intended for micropore analysis should be able to give similar results.

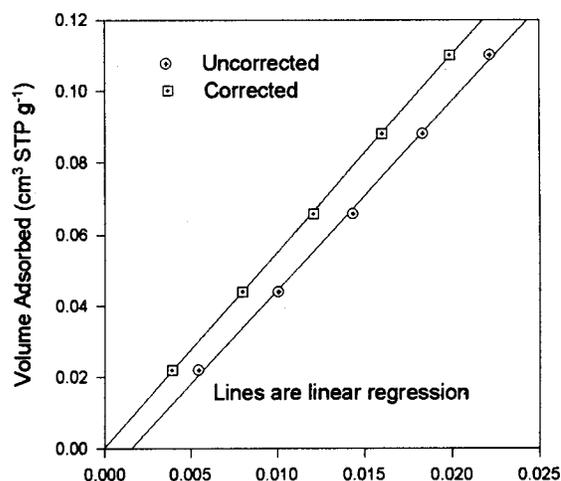


Figure 2. Nitrogen adsorption on uniform graphite surface showing expected Henry's Law behavior after correction for thermal transpiration effect.

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