A Simple and Inexpensive B.E.T. Apparatus

INTRODUCTION

The development of an accurate method for the determination of surface area by Brunauer, Emmett and Teller (*1*) was a crucial step in the development of surface science. Although there have been many improvements and modifications in the B.E.T. apparatus in the last thirty years (*2*, *3*), the usual apparatus is complex and, once built, is not the kind of instrument one entrusts to inexperienced students.

We have recently designed and built a much simpler apparatus for use by students with little or no experience in surface-area measurements. Although this apparatus is not capable of detecting very small amounts of adsorption, it is remarkably precise for the measurement of adsorption on solids with surface areas as low as about 2 m^2/g. Furthermore, the measurements can be made very rapidly, even by the beginner. The apparatus is inexpensive* and does not require accurate manometric scales, diffusion pumps, or large amounts of mercury.

APPARATUS DESIGN

A schematic diagram of the apparatus is shown in Fig. 1. In this type of apparatus, the adsorption isotherm is determined by varying the amount of adsorbate in the system by successive dosing rather than by varying the volume and pressure of a fixed amount of adsorbate, the method normally used in B.E.T. measurements. The essential feature of the apparatus is a Wallace and Tiernan gauge (model FA 160, 0–800 Torr) which is used to record the pressure in the system, to dose the adsorbing gas, and to measure the saturation vapor pressure of nitrogen. This eliminates the need for a calibrated mercury burette, a water jacket, and a manometric scale. The apparatus shown in Fig. 1, and the necessary pumping system, can be constructed for about $500.

For our particular system the dosing volume, the part of the apparatus indicated by the dashed box in Fig. 1, is 408 ml. It should be noted that this volume does not include the bores of stopcocks 2 and 3. The dosing volume was determined by attaching a known volume on the standard taper below stopcock 2, filling the system with helium at a known pressure (read on the gauge), evacuating the dosing volume and expanding the helium into this volume. This procedure was repeated at several pressures to get an accurate value for the volume. The volume of the bore of stopcock 2 and the standard taper below it was measured by filling this volume with mercury and weighing the mercury. The accuracy of the gauge was previously checked against an accurate mercury manometer, and the gauge was found to deviate by only 1–3 Torr at pressures below 75 Torr and above 700 Torr. Since accuracy probably varies from gauge to gauge, this should be checked if possible.

The connection of the gauge is made by epoxy resin from a pipe-thread elbow on the gauge directly to capillary tubing (*4*). The volume below stopcock 2 should be kept as small as possible by using capillary tubulation on the stopcock and a capillary standard taper. The tubulation on bulb A may be made out of a noncapillary standard taper, but a solid glass rod should be inserted into bulb A above the sample to reduce the dead space. The two bulbs, A and B, should be close together so they will fit into a half-pint or pint Dewar flask.

Small tanks of high purity helium and nitrogen are connected permanently by epoxy glass-to-metal seals from spirals of

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* After designing and building two models of the apparatus described in this paper, we learned that a commercial instrument of similar design is available for $2400 from NUMEC Corporation, Monroeville, Pa.

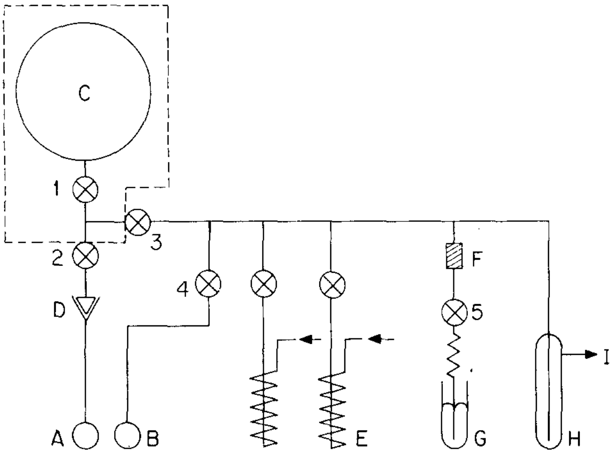

FIG. 1. Scheme of the apparatus: A, adsorption bulb; B, nitrogen thermometer; C, Wallace and Tiernan gauge; D, 10/30 standard taper; E, copper spiral cold traps connected to nitrogen and helium tanks; F, gold powder trap; G, safety manometer; H, cold trap; I, to mechanical pump.

$\frac{1}{8}$-in. copper tubing to a short manifold equipped with a mercury safety manometer designed to blow out at pressures above 800 Torr. The manometer should be equipped with a small gold powder trap above stopcock 5. The gases are passed slowly through the spirals at liquid nitrogen temperature to remove oil and water. Alternatively, the gases can be purified and stored in large bulbs attached to the manifold although we find this less convenient.

Rather than use a separate nitrogen thermometer to measure the saturation vapor pressure of nitrogen (P_0), we have incorporated an extra bulb (B in Fig. 1) which is used for the measurement in conjunction with the gauge. This procedure is described in the next section.

For most surface-area measurements, the apparatus as depicted in Fig. 1 is entirely adequate. For experiments which require high vacuum, a diffusion pump may be inserted between the cold trap and the mechanical pump. The apparatus may also WHITEY toggle valves replacing the glass be built mostly of metal with HOKE or stopcocks.

PROCEDURE

Since a description of B.E.T. theory, procedure, and calculations may be found easily (*1–3*), we have summarized here only the major differences which arise because of the design of the apparatus.

The gauge and bulb B are evacuated prior to a determination, and stopcocks 1 and 4 are then closed. A sample in bulb A, held securely in place with glass wool and a solid rod, is evacuated at elevated temperature to remove water, and a Dewar full to the top with liquid nitrogen is then placed around both bulbs so that bulb A is immersed to at least one-half the depth of the liquid nitrogen bath. With stopcocks 2 and 4 closed, enough nitrogen is admitted to the gauge so that the final relative pressure after adsorption will be about 0.05 (40–50 Torr). From the measured pressure, the known dosing volume, and room temperature, the initial amount of nitrogen may be calculated. This fixed amount of nitrogen is then expanded into bulb A by closing stopcock 3 and opening stopcock 2, and the equilibrium pressure is recorded. Equilibrium is usually attained in about 20 min after the first addition of gas and in about 10 min for further additions. From a knowledge of the dead volume in bulb A (see below) the amount of nitrogen removed from the gas phase, equal to the amount adsorbed, may be calculated. This procedure is repeated for several successive additions of nitrogen until a relative pressure of about 0.3 (200–250 Torr) is reached.

TABLE 1

Typical Results of Surface-Area Measurements

Sample	Description	Pretreatment	Dry sample weight, g	Surface area, m^2/g
1	Davison 980 Silica-Alumina	Outgassed 15 hr, 475°C	0.249	388
2	0.05% Cu on MgO	Outgassed 12 hr, 500°C	0.799	90
3	5% Cu on TiO_2	Outgassed 12 hr, 500°C	4.504	10

Gas additions to the gauge must of course be made with stopcock 2 closed. The Dewar should be topped up occasionally with liquid nitrogen while the isotherm is being taken to avoid changes in the dead volume at liquid nitrogen temperature.

After the surface-area measurements, the value of P_0 is immediately determined by building up a pressure of nitrogen of about 800 Torr in the gauge and bulb B and watching the pressure fall. When two or three further additions of nitrogen lead to the same equilibrium pressure in the system, liquid nitrogen is condensing in bulb B, and the gauge is reading P_0.

A sample weight which gives at least 50 m^2 total area is convenient to use since this gives pressure changes that are easily measured. For samples with relatively high areas, the sample size and therefore bulb A can be very small. One of the advantages of this apparatus is that for small samples the dead volume below stopcock 2 can usually be ignored since it is not significant compared to the dosing volume. Conversely, large samples of 5 g or more can easily be used since the dead volume will still be only a few percent of the dosing volume. In the latter case, however, the dead volume should be determined by helium expansion from the gauge into bulb A.

The calculations are much simplified if

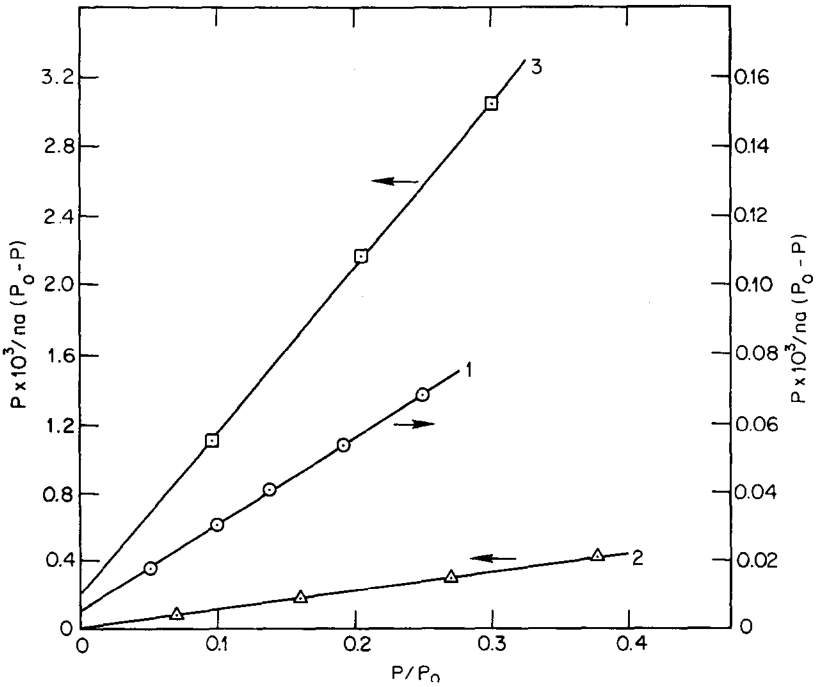

Fig. 2. B.E.T. plots for catalysts described in Table 1: P, equilibrium adsorption pressure in Torr: P_0, saturation vapor pressure of nitrogen in Torr; n_a, micromoles of nitrogen adsorbed per g of dry adsorbent.

the measurement of the dead volume is performed with the sample immersed in liquid nitrogen to the same depth as used during the determination of the isotherm. An amount of helium, n_0, is metered into the dosing volume. The helium is then expanded into the dead volume to give an equilibrium pressure, P_f, and the gas remaining in the calibrated volume, n_f, is calculated. The difference, $n_0 - n_f$, is the amount of helium which is in the dead volume at the pressure P_f. If the room temperature and the liquid nitrogen level do not change, the ratio $(n_0 - n_f)/P_f$, the dead volume factor, is a constant. The amount of nitrogen in the dead volume can be determined by multiplying each equilibrium pressure by this factor. We usually determine the dead volume factor at 3 or 4 helium pressures between 200 and 760 Torr and use an average value in the calculation. When samples are being used which are not sensitive to trace impurities in the helium, the dead volume and P_0 may be determined before the isotherm so that the results may be calculated immediately.

If a "cow" with stopcocks on the udders is attached to the standard taper, several samples can be pretreated at once and the surface areas determined successively in a short period of time.

RESULTS

We have successfully measured areas as low as 2 m^2/g and as high as 850 m^2/g by suitable adjustment of the sample weights. Table 1 and Fig. 2 give some representative data for three catalysts differing in surface area by a factor of almost 40 in the extreme. The results in Table 1 were calculated by assuming the area of a nitrogen molecule to be 16.2 Å^2. The surface areas of samples 1 and 2 were checked on a more sensitive conventional B.E.T. apparatus and found to be 388 and 93 m^2/g, respectively; these values are in excellent agreement with those reported in Table 1.

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