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# ADSORPTION AND VACUUM TECHNIQUE

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## PREFACE

In recent years surface chemistry and adsorption have taken on new interest for industry. Their growing importance is illustrated by their use in the purification of petroleum by chromatographic techniques, syntheses depending on contact catalysis, sugar refining, hydrogenation of oils, clay treatment of gasolines, and compounding of rubber articles. More recently they have come to be used in the study of thin films, semiconductors, semiconductor devices, and the development of the catalytic muffler. Within the last few years a tremendous effort has been made to apply the theories of semiconductors in linking the properties of solids to the heretofore classical fields of adsorption and surface chemistry.

For the sake of better understanding of the processes mentioned above, the surface properties of the adsorbent must be studied. The investigation of surface areas, pore volume distributions, total pore volumes, densities, and surface activities, along with kinetic experiments and such measurements as resistivity, thermoelectric power, magnetic susceptibility, nuclear magnetic resonance, and others, all lead to a better understanding of adsorbents and adsorption phenomena.

In 1955 C. B. Willingham and the author wrote "The Assembly, Calibration, and Operation of a Gas Adsorption Apparatus for the Measurement of Surface Area, Pore Volume Distribution, and Density of Finely Divided Solids."<sup>1</sup> Since that time many requests for copies have been received. Because of the continual interest in this subject, it was suggested that the original adsorption bulletin be revised. It was decided to revise the original work, which was concerned only with volumetric techniques, and to extend the discussion to a gravimetric technique.

The purpose of this report is to describe in some detail the assembly, calibration, and operation of a volumetric and a gravimetric gas-adsorption apparatus in such a way that this report may be used as a manual by those beginning adsorption studies, and also by others whose techniques and procedures may benefit from this presentation.

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# ADSORPTION AND VACUUM TECHNIQUE

## ABSTRACT

A volumetric adsorption apparatus and a gravimetric one are described. The discussion of the volumetric method includes a detailed description of the construction and calibration of the basic apparatus, typical sample tubes, a special dewar, a heater, and special control devices. The procedures and methods of calculating specific surface area by the B.E.T. method using both nitrogen and krypton, and of calculating true density, are presented step by step. The measurement of pore volume distribution is also discussed.

The gravimetric technique uses a quartz beam microbalance. The construction, manipulation, and calibration of the balance are described, along with procedures and calculations for typical measurements based on mass increases. These techniques include the measurement of sorption equilibrium, surface area, sorption kinetics, and magnetic susceptibility.

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## 1

### VOLUMETRIC APPARATUS FOR THE MEASUREMENT OF SURFACE AREA, PORE VOLUME DISTRIBUTION, AND DENSITY OF FINELY DIVIDED SOLIDS

#### 1.1. INTRODUCTION

This report describes the gas-adsorption apparatus used by the author in the work of the Department of Research in Physical Chemistry at the Mellon Institute for studies of the surface area, pore volume distribution, and density of a variety of finely divided and porous solids. A schematic diagram of the completed apparatus is shown, as are detailed drawings of several types of sample tubes, a manometer, a purification train, a special dewar, a constant level device, and a heater. The assembly, calibration, and testing of the gas-measuring system, the nitrogen thermometer, and the auxiliary systems for gas purification and transfer are discussed. The operation of the apparatus is explained, and the calculations and corrections for making typical measurements by use of nitrogen and krypton gases are given. A table listing values for the cross-sectional area per adsorbed particle of various adsorbates is included in an appendix. The determination of true density is discussed, and an illustrative example provided.

The adsorption apparatus and technique have been automated by Ballou and Doolen (Reference 1). This adaptation is excellent for the surface-area measurement of large numbers of samples having somewhat similar properties.



## 1.2. SURFACE AREA AND THE B.E.T. EQUATION

Adsorption is said to occur when a fluid (i.e., a gas or a liquid) comes into contact with a solid and some of the fluid tends to adhere in the form of layers of fluid molecules. This process is called physical adsorption when adhesion is caused by relatively weak forces such as van der Waals forces. It is called chemisorption when the forces at the solid-fluid boundary (i.e., the interface) are strong enough to promote chemical reaction (Reference 2, page 4). The magnitude of these forces, of course, varies from system to system, and there is no sharp dividing line between the energies of physical and chemical adsorption. It is physical adsorption which permits the calculation of surface area and pore volume distribution.

If the number of adsorbed molecules of a fluid which covers the adsorbent with a monomolecular layer could be determined, and if the area occupied by a single adsorbed molecule were known, the surface area available to the adsorbate molecules could be calculated. Since a method of calculating the area of an adsorbed particle has been described (Reference 3), the problem that remains is to calculate the number of molecules in a physically adsorbed monolayer.

Several treatments lend themselves to a theoretical explanation of specific adsorption data (References 4, 5, and 6), but until 1938 no really general treatment had been proposed. In that year Brunauer, Emmett, and Teller (B.E.T.) (Reference 7) proposed a theory of multimolecular adsorption from which a value for the monolayer could be calculated.

From the B.E.T. theory, the adsorption of a gas on a solid may be represented by the equation:

$$V = \frac{V_m Cx}{1-x} \left[ \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (C-1)x - Cx^{n+1}} \right] \quad (1)$$

where  $x$  is the relative pressure,  $P/P_0$ ,  $P$  is the equilibrium pressure and  $P_0$  is the saturation pressure;  $V$  is the volume of gas adsorbed at equilibrium;  $V_m$  is the volume adsorbed in a monolayer;  $n$  is the number of layers; and  $C$  is a constant related exponentially to the heat of liquefaction and the heat of adsorption (Reference 2, page 154).

When  $n = 1$ , Equation 1 reduces to Equation 2, the Langmuir equation:

$$\frac{V}{V_m} = \frac{kP}{1+kP} \quad (2)$$

where  $k$  is equal to  $C/P_0$ . When  $n$  is infinite,

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (3)$$

A plot of  $P/V(P_0 - P)$  with respect to  $P/P_0$  is usually linear over the range of relative pressures from 0.05 to 0.35 where the slope,  $S$ , is  $(C - 1)/V_m C$  and the intercept,  $I$ , is  $1/V_m C$ . Since

$$S + I = \frac{1}{V_m C} + \frac{C - 1}{V_m C} = \frac{1}{V_m}$$

then

$$V_m = (S + I)^{-1} \quad (4)$$

The specific surface may be calculated from the following relationship.

$$\text{specific surface} = \frac{V_m K}{\text{sample weight in grams}} \quad (5)$$

where  $K$  is a constant for each adsorbate and is calculated from Equation 6.

$$K = \frac{NA}{M_v} \quad (6)$$

where  $N$  is Avogadro's number,  $A$  is the area occupied by one adsorbate molecule, usually in the liquid state, and  $M_v$  is the gram molecular volume. For nitrogen and krypton at liquid-nitrogen temperatures,  $K$  is 4.38 and 5.28, respectively, when the specific surface is expressed in square meters per gram. Several authors (References 8 through 13) have endeavored to improve the theory of adsorption (and catalysis), with some success. It must be noted, however, that the equations derived from the B.E.T. theory still remain general enough to apply to most of the experimental data encountered. As a consequence, many experimenters use the B.E.T. method qualitatively as well as quantitatively to describe changes on the surface of the sorbent.

The volumetric adsorption apparatus is used not only to obtain data to compute a surface area, but also to obtain data necessary to calculate pore volume distributions, densities, and adsorption rates.

**1.2.1. PORE VOLUME DISTRIBUTION.** Reference 14 describes a technique by which the pore volume distribution in porous solids may be determined from adsorption data. Suitably corrected, the Kelvin equation (Equation 7) can be used to describe the pore volume distribution of a porous solid over a range of pore radii from 5 Å to 300 Å.

$$\ln \frac{P}{P_0} = \frac{-2\sigma V \cos \theta}{rRT} \quad (7)$$

where  $P$  and  $P_0$  are as before,  $\sigma$  is the surface tension of the adsorbate,  $V$  is the molal volume of the liquid adsorbate,  $\theta$  is the contact angle,  $r$  is the capillary radius,  $T$  is the absolute tem-

perature, and  $R$  is the gas constant. Since the experimental techniques applied in this measurement differ only slightly from those used to determine surface areas, some mention of the method will be made later.

1.2.2. DENSITIES. True densities of adsorbents may be obtained very easily with the gas-measuring system of the adsorption apparatus (Reference 15). Since helium is chemically inert and is not adsorbed at the operating temperature, it is an ideal displacing fluid. The densities calculated by use of helium are usually higher than values obtained by other techniques, because the dimensions of the helium atom permit it to penetrate into pores too small to be accessible to many commonly used displacing liquids such as benzene or toluene.

1.2.3. KINETIC MEASUREMENTS. The apparatus that will be described below is very versatile and may be used for other studies and purposes with only slight modification. Kinetic studies of the rate of uptake of a gas by a solid may be made if the rate of uptake is not too rapid. The apparatus, then, is used as a constant-volume system. To use it as a constant-pressure apparatus, one must provide a manostat arrangement (Reference 16) or change the volume of the system. Frequently this is difficult to do.

### 1.3. ASSEMBLY OF THE ADSORPTION APPARATUS

The complete apparatus is diagramed in Figure 1. It consists of a system of four interconnected units: the sample tube, burettes, manometer, and mercury reservoirs; the gas-purification train and the gas storage reservoirs; the nitrogen thermometer and its manometer; and a high vacuum source (not shown) that consists of a mechanical pump, a diffusion pump, and a cold trap. Each of these units can be isolated from the others.

The apparatus was arranged for easy access to all of its parts, particularly the most frequently used stopcocks. It was mounted on a frame equipped with service lines for gas, water, air pressure, and electricity.

The individual pieces of the apparatus (other than stopcocks) in Figure 1 are lettered. The letters have the following significance.

- |       |  |
|-------|--|
| A     | Sample tube  |
| B, B' | Gas burettes, calibrated, for measuring the working volumes of gas                 |
| C     | Manometer used to measure the gas pressure over the sample and in the gas burettes |
| D     | Mercury reservoirs for the manometer and the burettes                              |
| E     | Fine pressure control for manometer C (Reference 17, page 261)                     |

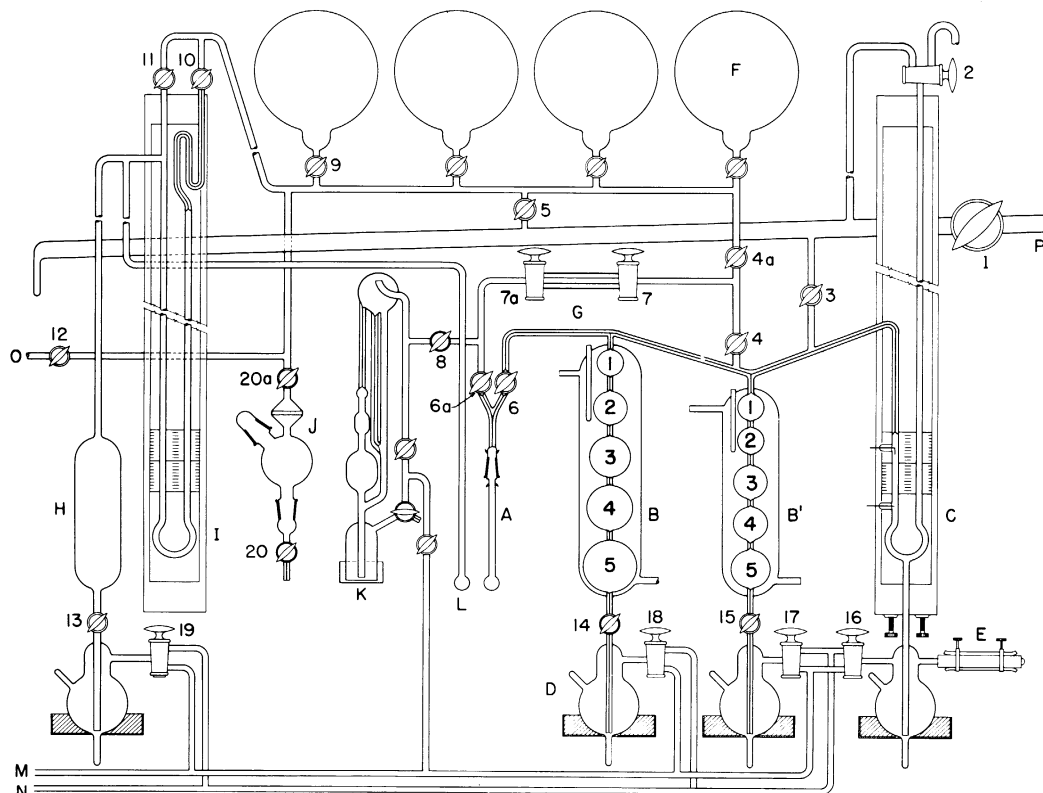


FIGURE 1. SCHEMATIC DIAGRAM OF THE GAS-ADSORPTION APPARATUS

- F Gas reservoirs, 3-liter capacity, for storage of purified gases
- G Calibrated doser for measuring quantities of (krypton) gas
- H Uncalibrated gas holder, used to compress gas enough to produce liquid-vapor equilibrium in the nitrogen thermometer bulb at liquid-nitrogen operating temperatures
- I Manometer of gas thermometer system
- J Drying tube filled with anhydrous calcium sulfate (Drierite)
- K Calibrated McLeod gauge for krypton system and general usage
- L Gas thermometer bulb
- M To mechanical oil pump
- N To source of air pressure, about 15 psig
- O To traps and purification train
- P To high vacuum source

The stopcocks shown in Figure 1 were equipped to operate under pressure or vacuum. They are identified in the figure and in the text by numbers which have the following significance.

- |                |   |
|----------------|---|
| 1              | 10-mm straight-bore stopcock; connects high vacuum source and gas-adsorption apparatus  |
| 2              | 4-mm oblique-bore three-way stopcock; used to equalize pressure on the legs of manometer (C); also used in producing Torricellian vacuum required in the right leg of the monometer |
| 3              | 2-mm oblique-bore capillary stopcock; connects gas-measuring system to vacuum   |
| 4              | 2-mm oblique-bore capillary stopcock; used to introduce gas from the reservoirs into the gas-measuring system   |
| 4a             | 2-mm oblique-bore stopcock; isolates krypton system from gas reservoirs   |
| 5              | 4-mm oblique-bore stopcock; for evacuating reservoirs, F, and gas-purification train  |
| 6, 6a          | 2-mm oblique-bore three-way capillary stopcocks; connect sample tube to the gas-measuring systems (see text)  |
| 7, 7a          | 2-mm oblique-bore three-way capillary stopcocks of the krypton doser, G   |
| 8              | 4-mm oblique-bore stopcock used to isolate McLeod gauge   |
| 9              | 4-mm oblique-bore stopcocks of gas reservoirs, F  |
| 10             | 2-mm oblique-bore capillary stopcock to the vacuum leg of manometer I   |
| 11             | 4-mm oblique-bore stopcock; used to evacuate the thermometer system and to fill this system with gas  |
| 12             | 4-mm oblique-bore three-way stopcock; diverts gas flow from either of the cold traps in the purification train into a single line connected to the gas reservoirs                   |
| 13, 14, 15     | 2-mm oblique-bore capillary stopcocks used as fine controls of the flow of mercury between the mercury reservoirs and the burettes  |
| 16, 17, 18, 19 | 2-mm oblique-bore three-way capillary stopcocks; pressure-vacuum controls for the mercury reservoirs  |
| 20, 20a        | 4-mm oblique-bore stopcocks; outlet to atmospheric pressure through drying tube J   |

Only stopcocks specially ground for high vacuum should be used; these should be held by some means to permit the use of pressure as well as vacuum.<sup>2</sup>

All connecting lines are 10-mm o.d. (outside diameter) tubing, except as indicated in Figure 1.

The burettes, reservoirs, and manometers are custom made, and can be readily constructed from stock items of Pyrex glassware if adequate glass blowing facilities are available. The components of the high-vacuum system, including traps, oil- or mercury-vapor diffusion pumps, vacuum gauges, and mechanical fore pumps, are available from laboratory supply houses.

1.3.1. SAMPLE TUBES. Various types of sample tubes may be used with the adsorption apparatus. The surface area and density of the sample material dictate the size and shape of the

<sup>2</sup>Excellent precision-ground stopcocks may be purchased from Eck and Krebs Co., Long Island City, N. Y.; a universal stopcock adaptor, supplied by the Emil Greiner Co., N. Y., permits safe pressure and vacuum operation of stopcocks.

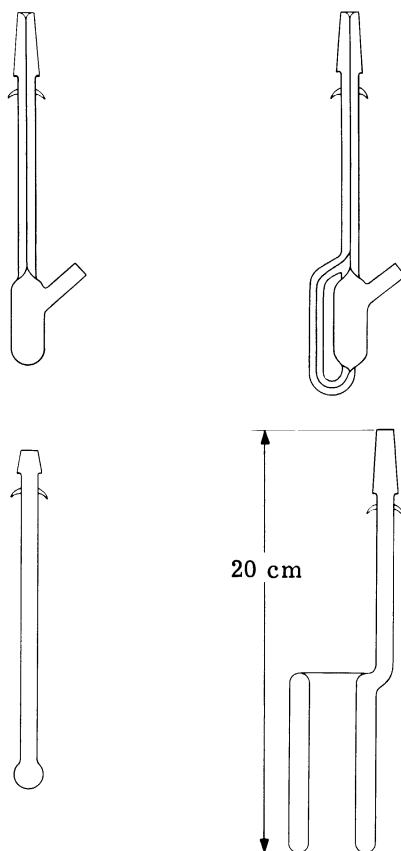


FIGURE 2. TYPICAL SAMPLE TUBES

sample tube to be used. Four typical sample tubes, drawn to scale, are shown in Figure 2. In tubes (a) and (b), the sample is introduced through the open side arm into the bulb and the side arm sealed; after the tube is filled with finely divided materials and the side arm is sealed, a glass-wool plug is placed in the capillary shank. Tube (b) is similar to (a) except that it provides for evacuation on two sides of a sample plug. Tube (c) eliminates glass working by the operator. First it is filled with the sample; then a glass-wool plug is set in place, and the excess volume in the connecting tube is filled with a close-fitting rod. Tube (d), designed to surround the gas thermometer bulb, is used primarily for density determinations. It may also be used for surface-area estimations of low-area materials, in which nitrogen is used as the adsorbate. All tubes shown are provided with a connection to a 10/30 standard taper joint or joints adaptable to 10/30 and are constructed from Pyrex or Vycor glass.

1.3.2. BURETTES. The measuring burettes are similar to those described by Joyner (Reference 17, page 261). Burette B has a total volume of 250 ml (10-, 15-, 25-, 50-, and 150-ml

bulb volumes). Burette B' is optional; it has a total volume of 50 ml, and bulb volumes of 5, 5, 10, 10, and 20 ml, respectively.

Distilling flasks provide a convenient source of bulbs suitable for the construction of burettes. Calibration lines are etched between bulbs and at the ends of each bulb train. Before the burette is mounted, the volume of each bulb is determined by weighing, at constant temperature, the volume of mercury between appropriate lines etched on the bulbs. Weighings to five significant figures are sufficient. The burettes are mounted securely before they are sealed into the system. A constant-temperature bath should be connected to the burettes if room temperature varies more than  $\pm 1^{\circ}\text{C}$  during the operating period.

1.3.3. BURETTE-SYSTEM MONOMETER. The tungsten-through-glass electrical contacts of the burette monometer (C in Figure 1) are drawn in detail in Figure 3. The upper wire is

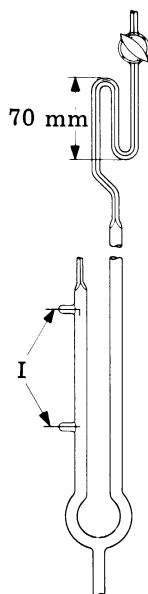


FIGURE 3. DETAILS OF MERCURY SEAL AND ELECTRICAL CONTACTS FOR THE MANOMETERS

bent at right angles, and the vertical portion is centered in the tube. This tungsten contact is made pointed by grinding or by chemical treatment while hot with sodium nitrite. The contacts, I, should be cleaned by electrolysis in dilute alkali solution before the manometer is permanently mounted. The manometer is mounted on a wooden support which has a flush-mounted, millimeter-scaled mirror. The position of the mirror is adjusted, by means of machined screws at the bottom of the mount (Figure 1), so that an appropriate scale division coincides with the up-

per tungsten pointer. Provision is made for a small 1/25-watt neon indicator lamp (NE-51) in the vicinity of the upper tungsten contact. The 115-volt a-c electrical circuit consists of the neon lamp, a 200,000-ohm 1-watt resistor, and the electrodes connected in series. The lamp can be made to flicker by gently tapping the manometer when the Hg inside it is almost touching the upper tungsten contact. An "electric eye" vacuum-tube circuit (Reference 17, page 276) is often used as an alternative.

An S-shaped capillary tube is placed at the top of the right arm of the manometer, as illustrated in Figure 3 (Reference 18). This device is used to set the vacuum leg of the manometers, and eliminates the necessity of constant pumping of the vacuum leg. To set the manometer, mercury is forced up the leg through the capillary S-tube and the stopcock. This stopcock is then closed, and the mercury is allowed to return to the manometer reservoir. Tapping the S-tube gently as the mercury begins to recede causes the mercury thread to separate in the S and form a seal. Conveniently, leaks through the stopcock can be detected as a change in the mercury levels in the S-tube.

1.3.4. PURIFICATION TRAIN. Gases used for all measurements should have at least 99.99% purity. This may be achieved by use of the simple gas-purification train illustrated in Figure 4. Gas enters at A and is directed to flow through either trap or both in series, as desired.

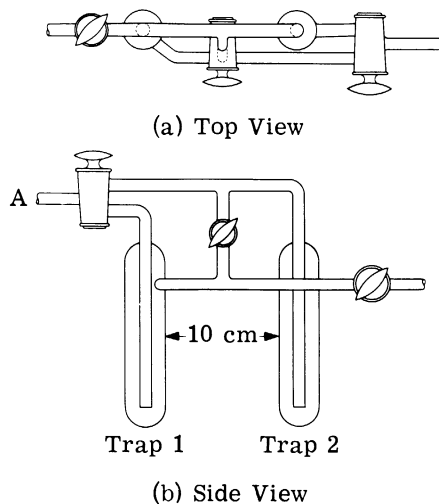


FIGURE 4. GAS-PURIFICATION TRAIN

In use, trap 1 is filled with 3/16-inch glass beads and trap 2 with adsorbent-grade coconut charcoal, 18 to 28 mesh. When the trap has cooled to liquid-nitrogen temperature, water and other condensable impurities are removed from the helium and nitrogen before they are stored in the reservoirs (F in Figure 1). The glass beads are used for nitrogen purification, and the



charcoal for helium purification. Other purifying agents (Reference 17, page 272, and References 19 and 20) may replace or supplement those mentioned to eliminate specific impurities from the adsorbate.

1.3.5. MERCURY RESERVOIRS. The mercury reservoirs shown as D in Figure 1 are constructed from 500-ml round-bottom flasks. Tubes are fashioned at the side and bottom to facilitate changing the mercury. Each reservoir is supported by a plaster-of-Paris mold in a brass dish. A 1/2-inch o.d. brass rod is attached to the dish and clamped to the frame with standard clamp holders. When filled, the reservoirs are used to supply mercury to the burettes and manometer. This is done by applying air pressure or vacuum to the mercury surface in the reservoir through stopcocks 16-19. Before the mercury reservoirs are operated, they should be wrapped with masking tape or an electrical insulating tape, to prevent injury to the operator in case the reservoir breaks.

1.3.6. GAS RESERVOIRS. The four gas reservoirs, F in Figure 1, are constructed from 3-liter round-bottom flasks. One reservoir is used for helium and the other three for adsorbate gases, nitrogen, oxygen, etc. Before the reservoir is charged, it is connected through stopcocks 9 and 11 to manometer I, and evacuated through 5. Then, with stopcock 5 closed, gas enters through 12 from the purification train, O. When a pressure of about 900 mm is obtained on manometer I, stopcock 9 is closed and the excess gas in the train is then pumped off. By keeping the pressure in the reservoirs above atmospheric pressure, contamination of the adsorbate gases with air is minimized. For safety, each reservoir should be wrapped with masking tape and spray-coated with a tough plastic film (Krylon). Krypton is supplied in 1-liter Pyrex flasks that can be sealed directly to the system between stopcocks 4 and 7.

1.3.7. THE DEWAR FLASK. A dewar flask convenient for use with liquid nitrogen is shown in Figure 5. Its capacity is approximately 1.5 liters. The neck of the flask is narrowed as shown to prevent rapid loss of the refrigerant. In the figure, A is 1/2-inch Transite, B is 1/6-inch aluminum, G is Pyrex glass, and H is a sealing wax (Apiezon-W). The dewar is wrapped with 1-inch masking tape and sprayed with a plastic as a safety measure.

In order to prevent the condensation of atmospheric oxygen in the dewar when using liquid nitrogen, and to maintain a relatively stable bath temperature, the mouth of the dewar is covered and pure dry nitrogen is bubbled through the liquid-nitrogen bath at a rate of about 25 bubbles per minute. This procedure also minimizes density inversions within the bath, which sometimes cause large and unexpected changes in the value of  $P_0$ .

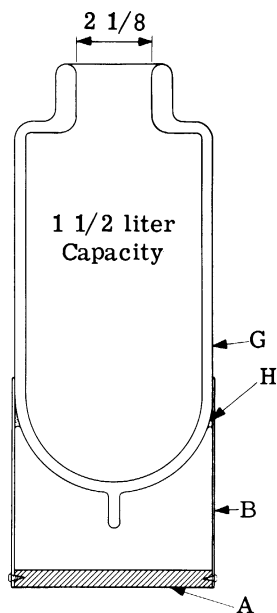


FIGURE 5. DEWAR FLASK FOR  
USE AS A LIQUID-NITROGEN  
BATH

1.3.8. CONSTANT-LEVEL DEVICE. A modification of a device described by Feld and Klein (Reference 21) is used to maintain a constant level in the liquid-nitrogen bath. It is shown diagrammatically in Figure 6, where the letters have the following significance.

- A Liquid-nitrogen reservoir
- B Transfer tube with silvered and evacuated jacket
- C Level-sensing bulb, air-filled
- D Mercury manostat
- E Dewar with level of liquid nitrogen controlled

As used here, the manometer shown replaces the somewhat more complex valve system used by Feld and Klein. With a 4-liter reservoir, this system can maintain the level in the liquid-nitrogen bath within 5 mm for 36 hours. Thus a complete isotherm determination lasting two days, can be carried out with no danger that the sample will warm to above the bath temperature while unattended overnight.

1.3.9. THE HEATER. A heating unit suitable for degassing samples at elevated temperatures is constructed by winding Nichrome resistance wire around an Alundum tube and applying proper insulation. A scale drawing of the heater, showing the details and materials of construc-

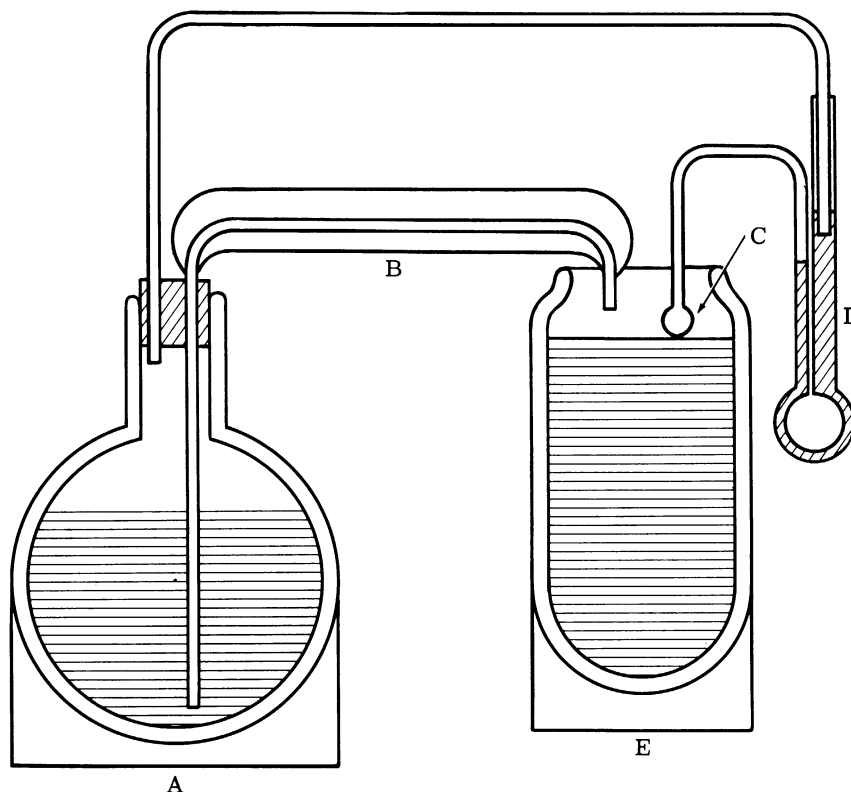


FIGURE 6. DEVICE FOR CONTROLLING LIQUID LEVEL OF NITROGEN BATH

tion, is shown in Figure 7, where A is 1/2-inch Transite, B is 1/16-inch aluminum, C is an appropriate insulating material, D is a 3/8-inch grooved Alundum tube, E is a porcelain electrical insulator, and F is the insulated leads of the resistance heater unit (B and S No. 22 Nichrome wire). A mercury-in-glass thermometer or a thermocouple, placed in the heater near the sample tube during an evacuation, is used to determine the bake-out temperature.

#### 1.4. CALIBRATIONS AND BULB FACTORS

Before any measurements are attempted with the apparatus, it must be proven to be vacuum tight. Upon completion of the glass working, the ground joints are sealed with a lubricant such as Apiezon N.<sup>3</sup> All atmospheric exits are closed, and the apparatus is evacuated by the mechanical vacuum pump. A high-frequency vacuum tester is used to check the entire system for imperfections in the sealed glassware. If no "pinholes" are found, the system is pumped under high vacuum (diffusion pump) for several days to remove water and adsorbed gases. Flame

<sup>3</sup>Product of Metropolitan-Vickers Electrical Co., Ltd., available through James G. Biddle Co., Philadelphia 7, Pa.

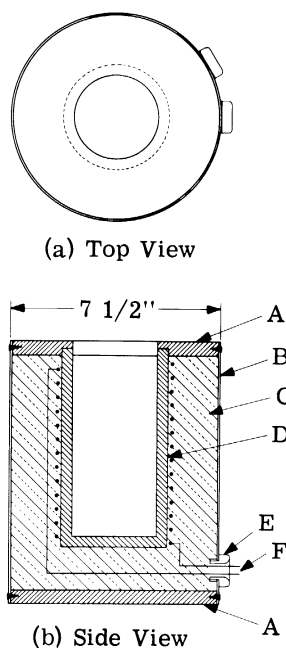


FIGURE 7. DETAILED DRAWING  
OF THE HEATING UNIT

brushing of the connecting lines with an air-gas flame aids in this process. After the water is removed, all stopcocks are closed and the apparatus is allowed to equilibrate for 24 hours. Leaks caused by faulty greasing of ground joints are found by noticing changes in manometer C when the various units are connected. Faulty stopcocks can be quickly isolated and regreased. If pinholes or faulty ground joints are found, the above procedure is repeated after the necessary repairs. The mercury reservoirs are then filled with triple distilled mercury. The quantity of mercury added is approximately 1 1/2 times that needed to fill the piece of apparatus served by the reservoir.

The section of capillary connecting stopcock 6 to burettes B and B' and to the top of the upper tungsten contact of manometer C is the zero bulb volume. Since it is a part of the working system, its volume must be calibrated. Gas calibration according to simple pressure-volume relationships is recommended. Stopcocks 3, 4, and 6 are closed. The mercury in each burette is set at the top etched line (zero bulb volume). Helium is introduced through stopcock 4 until the manometer registers a pressure of about 500 mm. No. 4 is closed and the manometer is zeroed at the upper tungsten contact by use of the fine adjustment and the indicator lamp. The pressure of an unknown quantity of gas of volume X is read and recorded as  $P_1$ . The mercury is lowered to the second etched line (bulb volume 1B), the manometer is zeroed again, and the pressure  $P_2$  corresponding to a new volume is recorded.

At constant temperature the following relationship is valid:

$$P_1 X = P_2 (X + Y)$$

or

$$X = P_2 Y / (P_1 - P_2) \quad (8)$$

Y is the volume of the first bulb as determined by weighing with Hg. The zero bulb volume may be checked by determining the pressure at another bulb volume such as 2B. An alternative method of determining the zero bulb volume is discussed by Joyner (Reference 17).

To facilitate computations of volumes of gases at standard conditions, a table of conversion factors for both burettes, such as Table I, is prepared for each bulb setting and for each combination of bulbs. A volume of gas measured under one set of conditions can easily be converted to its volume at standard conditions by use of Equation 9:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or

$$V_2 = \frac{P_1 V_1}{T_1} \cdot \frac{T_2}{P_2} = \frac{P_1}{T_1} \cdot F_v \quad (9)$$

TABLE I. BULB FACTORS\*

Bulb	Nitrogen					
	Zero	1B'	2B'	3B'	4B'	5B'
Zero	2.991	4.551	6.041	9.244	12.581	19.252
1B	6.594	8.154	9.644	12.847	16.184	22.252
2B	11.886	13.446	14.936	18.139	21.476	28.147
3B	20.853	22.413	23.903	27.106	30.443	37.114
4B	38.167	39.727	41.217	44.420	47.757	54.428
5B	90.075	91.635	93.125	96.328	99.665	106.336

Krypton

McLeod system 58.71

Upper doser tube 0.2583

Lower doser tube 0.6372

\*These sets of factors, applicable only to the apparatus used at the Mellon Institute Laboratory, are used in the illustrative examples which follow.

where subscripts 2 and 1 denote standard and operating conditions respectively

$F_v$  is the bulb factor, defined as

$$F_v = V_1 \cdot \frac{T_2}{P_2} \cdot \frac{D_{25}}{D_0} \quad (10)$$

$V_1$  is the accumulative volume of the bulbs

$T_2$  is 273.16°K

$P_2$  is 760 mm Hg

$D_0$  is the density of mercury at 0°C

$D_{25}$  is the density of mercury at 25°C, or more correctly,  
the operating temperature of the bulbs

A table of factors may then be constructed by substituting the appropriate values in Equation 10. Three tables of factors may be constructed that use density values of mercury at 20°C, 25°C, and 30°C. In practice one uses the table most nearly corresponding to the operating bulb temperatures. The nitrogen adsorption system is now completely calibrated and ready for adsorption measurements.

#### 1.5. DETERMINATION OF SURFACE AREAS FROM NITROGEN ADSORPTION

Before the surface area can be determined from nitrogen adsorption isotherms, three preliminary operations must be performed. These include selecting the sample, outgassing the sample, and determining the dead space.

1.5.1. SELECTING THE SAMPLE. It is advantageous to know the approximate area of the material in question in order to determine the quantity of sample needed for a determination. If the surface area cannot be estimated, it is recommended that a 0.5-gram sample<sup>4</sup> be used with an initial charge of 30 cc of nitrogen. For the burette system described, these quantities will be sufficient for a determination of areas between 10 and 500 m<sup>2</sup>/gram, or at least will serve in a trial run for estimating the adsorption capacity of the sample. With nitrogen as the adsorbate, equilibrium pressures in the range 40 to 280 mm Hg will be needed for a determination. Table II serves as a rough guide to the amount of sample to be taken. In a burette system having a total operating volume of about 300 cc, it is convenient to use a nitrogen volume of approximately 30 to 40 cc at standard conditions. The sample needed for a measurement of surface area using

<sup>4</sup>Sampling techniques are available which provide means of obtaining representative samples (Reference 22).

TABLE II. SIZE OF SAMPLE AND QUANTITY OF NITROGEN USED, BASED ON AN ESTIMATED SPECIFIC SURFACE

Estimated Specific Surface ( $\text{m}^2/\text{gram}$ )	Sample Size (grams)	Volume of $\text{N}_2$ at S.T.P. (cc)
1	3-4	30
10	2-3	30
100	0.5-1.0	30
500	0.2-0.3	30
700	0.1-0.2	30-40
1000	0.1	40-50

nitrogen increases rapidly as the specific surface decreases to below  $1 \text{ m}^2/\text{gram}$ . It is advisable, as will be explained later, to use other gases, such as krypton, methane, ethane, etc., as the adsorbate gas for areas much less than  $1 \text{ m}^2/\text{gram}$ .

**1.5.2. REMOVAL OF ADSORBED WATER AND CONDENSABLE VAPORS.** Before an adsorption isotherm can be taken, adsorbed vapors must be removed from the surface of the sample, usually by evacuation at high temperature. Typically, the sample is heated under continuous evacuation at  $200^\circ\text{C}$  for two hours. No specific conditions will cover all materials. If the material is unstable toward heat or the adsorbed vapors desorb slowly, the conditions of temperature and time must be altered to clear the surface without changing the area.

With hydrated and temperature-sensitive, highly porous materials, special temperatures and evacuation periods must be used; otherwise the areas will be changed by decomposition of the hydrate or sintering of the porous material.

**1.5.3. DETERMINATION OF THE DEAD SPACE WITH HELIUM.** The volume of gas present in the free space of the sample tube at standard conditions, and not adsorbed by the sample at equilibrium, is used in calculating the volume of gas adsorbed. This volume must be measured at the adsorption temperature. Helium is used to determine this volume, because it is chemically inert and does not adsorb appreciably even at liquid-nitrogen temperature (Reference 23). The procedure for measuring the dead space is the same for most gases and adsorbents.

With a sample attached to the apparatus and properly baked out and under vacuum, the sample tube is isolated from the burette system by closing stopcock 6. Approximately 30 cc of helium is admitted to the burette system (4B bulb, 230 mm Hg pressure) through stopcock 4. The volume of gas taken is determined by noting the pressure in the burettes at two different bulb volumes, such as 4B and 3B, and using Equation 9. An appropriate cold bath is then placed

around the sample tube. Stopcock 6 is opened, and the helium is allowed to expand into the sample tube. When thermal equilibrium is established, the pressure is read and the volume of helium (S.T.P.) remaining in the burette system is calculated. The volume of helium present in the sample tube is the difference between the total helium and the quantity remaining in the burette system at the equilibrium pressure. The ratio of the volume of helium in the sample tube divided by  $P_c$  is a constant.  $P_c$  is the equilibrium pressure, corrected to  $0^\circ\text{C}$  by multiplying the observed pressure by the ratio of the density of mercury at  $0^\circ\text{C}$  to its density at  $T_B$ . The constancy of this ratio, the dead-space factor  $F_s$ , can be checked by changing the volumes in the burettes and obtaining different equilibrium pressures. The magnitude of the dead-space factor is preferably of the order of 0.001 to 0.01 cc/mm; it varies as the volume of the dead space surrounding the sample.

Before proceeding with the area measurement, the helium gas must be removed from the adsorption system.

**1.5.4. MEASUREMENT OF THE ISOTHERM.** When the sample has been prepared for nitrogen adsorption, the dead-space factor determined, and the sample tube and burette system evacuated, stopcocks 6, 4, and 3 are closed; an appropriate volume of nitrogen (see Table II) is admitted to the burette system through stopcock 4, which is then closed. The mercury is adjusted in manometer C, and the pressure is read and recorded. The burette temperature is also recorded. A check determination of the volume is made by adjusting the mercury in the burette to a different level and recording the new pressure. The pressures and temperatures are used in Equation 9 to determine the initial charge of nitrogen at standard conditions. With the liquid-nitrogen bath in place around the sample tube, stopcock 6 is slowly opened. The pressure will decrease as the nitrogen expands into the evacuated sample tube and adsorption begins. The mercury in the burettes is adjusted to produce a pressure near 100 mm Hg, and the system is allowed to equilibrate. When equilibrium is reached, no further decrease in the pressure is observed; the pressure,  $P$ , the burette bulb used, the burette temperature,  $T_B$ , and the vapor pressure of nitrogen,  $P_0$  (I in Figure 1), at the liquid-nitrogen bath temperature are recorded.

In operation, the gas thermometer system (H, I, and L in Figure 1) is filled with the particular adsorbate being used, if the condensed adsorbate has a vapor pressure greater than 10 mm Hg at the operating bath temperature. (An alternative method of determining  $P_0$ , described in Section 1.1.6, may be used if the vapor pressure of the condensed adsorbate is below 10 mm Hg.) To fill the gas thermometer system with nitrogen, a few milliliters of mercury are first run into H through stopcock 13. The gas thermometer system is then evacuated through stopcocks 10 and 11. When evacuation is complete, stopcock 10 is closed. Nitrogen is admitted from reservoir F



through stopcock 11 until a pressure difference of 500 mm Hg is reached in manometer I; then stopcock 11 is closed and the excess nitrogen pumped off through stopcock 5. The vacuum leg of manometer I is set by a procedure similar to that for setting manometer C. To determine  $P_0$  for nitrogen, a liquid-nitrogen bath is placed around the thermometer bulb L, and H is filled with mercury until nitrogen begins to condense in bulb L. Condensation takes place between 750 and 850 mm Hg, according to the temperature of the liquid-nitrogen bath.  $P_0$  is then determined as the difference in the heights of the mercury in manometer I.

The volume in the burettes is then reduced by changing the mercury level so that a bulb combination occurs which causes the pressure in the system to increase by about 30 to 40 mm Hg. When equilibrium is again established, another set of data, i.e., pressures, burette volume, and burette temperature, is recorded. The above procedure is repeated until three sets of data in the desired range ( $P/P_0 = 0.05$  to  $0.35$ ) are obtained. If a complete isotherm is desired, data must be taken at intervals until the value of  $P/P_0$  is approximately 1.0. A plot in which the volume adsorbed per gram is taken as ordinate and the relative pressure ( $P/P_0$ ) is taken as abscissa shows characteristics which are specific for certain materials. Characteristic isotherms are given by Reis (Reference 24). Also, from such a plot the specific surface may be determined by the point B method described by Emmett et. al. (Reference 25). By this technique the quantity  $V_m$  may be directly determined by extrapolating the linear portions of the isotherm to zero relative pressure. However, this method is not applicable for all adsorbent-sorbate combinations and consequently is employed only when the B.E.T. plot over the specific range of relative pressures is nonlinear.

1.5.5. TABULATION OF DATA AND CALCULATIONS. The following is an example of the recorded data and the calculations used in determining the quantity of gas adsorbed in a monolayer,  $V_m$ . Tables III and IV are offered as convenient guides for recording data and calculations for the determination of  $V_m$  of a typical adsorbent. Table IV represents, line for line, values calculated from the data of Table III.

The columns in Table III are arranged as follows:

- B Gas employed
- C Position of stopcock 6
- D Burette bulb in use
- E Equilibrium pressure
- F Equilibrium pressure corrected to  $0^\circ\text{C}$
- G Temperature of the burette system
- H Pressure reading of the nitrogen (gas) thermometer

TABLE III. DATA FOR NITROGEN ADSORPTION\*

A Line	B Gas	C Stopcock 6	D Burette Bulb	E Observed Pressure, P (mm Hg)	F Corrected Pressure, P <sub>c</sub> (mm Hg)	G Temperature T <sub>B</sub> (°C)	H Nitrogen Vapor Pressure, P <sub>0</sub> (mm Hg)
(Dead-Space Determination)							
1	He	closed	4B	171.3		22.2	
2	He	closed	3B	313.8		22.2	
3	He	open	3B	251.8	250.6	22.4	
4	He	open	4B	151.0	150.3	22.4	
(Adsorption Measurement)							
5	N <sub>2</sub>	closed	4B	225.1		22.6	
6	N <sub>2</sub>	closed	5B	95.2		22.6	
7	N <sub>2</sub>	open	4B + 5B'	107.9	107.4	22.8	846.0
8	N <sub>2</sub>	open	4B	144.0	143.3	22.8	848.3
9	N <sub>2</sub>	open	3B + 3B'	187.2	186.3	22.8	843.3

\*Sample weight = 0.5976 grams.

TABLE IV. WORK SHEET FOR CALCULATING B.E.T. VARIABLES

A Line	B V <sub>t</sub>	C V <sub>b</sub>	D V <sub>s</sub>	E V <sub>a</sub>	F P/P <sub>0</sub>	G 1 - P/P <sub>0</sub>	H V <sub>a</sub> (1 - P/P <sub>0</sub> )	J P/V <sub>a</sub> (P <sub>0</sub> - P)
1		22.14						
2		22.15						
3	22.15	17.77	4.38					
4	22.15	19.50	2.65					
5		29.05						
6		28.99						
7	29.02	19.84	1.90	7.28	0.1275	0.8725	6.35	0.0200 <sub>8</sub>
8	29.02	18.57	2.55	7.90	0.1698	0.8302	6.56	0.0258 <sub>8</sub>
9	29.02	17.15	3.32	8.55	0.2220	0.7780	6.65	0.0333 <sub>8</sub>

$$F_s = \frac{\text{Column D}}{P_c} = 0.0176 \text{ cc/mm}$$

In Table IV, Columns B and C represent  $V_t$ , the total volume of gas taken, and  $V_b$ , the volume of gas remaining in the burettes at the equilibrium pressure. These volumes are calculated from Equation 9. Column D records  $V_s$ , the volume of gas present in the sample tube and not adsorbed.  $V_s$  is calculated from Equation 11.

$$V_s = (P_c) (F_s) (\beta) \tag{11}$$

$P_c$  is the equilibrium pressure corrected to 0°C,  $F_s$  is the free-space factor, and  $\beta$  is a correction for the nonideality of nitrogen (Reference 26) (Figure 8). Column E records  $V_a$ , the volume of gas adsorbed. It is obtained by subtracting the values in Columns C and D from those in Column B, i.e.,

$$V_a = V_t - V_b - V_s \tag{12}$$

Column F records  $P/P_0$ , the relative pressure, and is obtained by dividing the value in Column E of Table III by that in Column H. Columns G, H, and J then follow directly.

If  $P/P_0$  is plotted against  $\frac{P}{V_a(P_0 - P)}$  (Figure 9), a straight line which has an intercept I and a slope S is obtained. From the values of the slope and intercept,  $V_m$  is calculated from Equation 4. The area is then computed from Equation 5.

For the example given in Table III, Table IV, and Figure 9,  $V_m$  is found to have a value of 7.02 cc. If this value is substituted into Equation 5, a value for the specific surface of 51.5 m<sup>2</sup>/g is obtained.

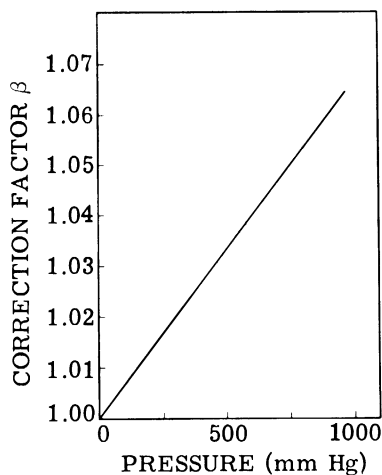


FIGURE 8. THE CORRECTION FACTOR,  $\beta$ , FOR THE NONIDEALITY OF NITROGEN AT LIQUID-NITROGEN TEMPERATURES

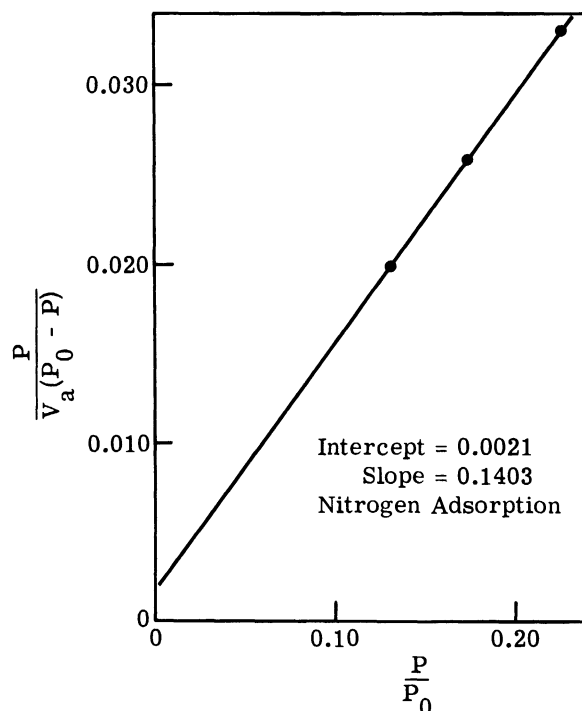


FIGURE 9. PLOT OF B.E.T. VARIABLES FOR DATA IN TABLE IV

#### 1.6. DETERMINATION OF SURFACE AREAS FROM KRYPTON ADSORPTION

The use of nitrogen as the adsorbate in determining specific surface area is practical when the samples have specific surface areas in the range of 1 to 2000 m<sup>2</sup>/g. But if the specific area of the material is less than 1 m<sup>2</sup>/g, considerable error results. The reason is that the volume of gas adsorbed,  $V_a$ , is small in comparison to the volume of gas in the sample tube at the relative pressures needed in the calculations. It is impossible to reduce the free space in the sample tube beyond some minimum value. It remains then to reduce the quantity of gas not adsorbed by the sample so that  $V_a$  is relatively large compared to the amount of gas remaining in the sample tube and not adsorbed at the desired relative pressure.

The first set of equilibrium data is usually taken at a relative pressure of 0.1. In order to reduce the quantity of gas not adsorbed, the pressure  $P$  must be reduced; but then the ratio of  $P/P_0 = 0.1$  decreases unless the value of  $P_0$  diminishes accordingly.

Vapors such as water, propyl alcohol, heptane (Reference 27), ethane, ethylene (Reference 28), and others (Reference 29) have been suggested as possible adsorbates in the low-area region, and have been used. However, their use involves various techniques not readily available

to many laboratories. Krypton, suggested by Beebe et al. (References 30 and 31) as a satisfactory adsorbate, has been found suitable for specific surface measurements because the correction for unadsorbed gas is kept low by the low saturation pressure of liquid krypton at liquid-nitrogen temperatures. The technique of making pressure measurements, though more refined than that used for nitrogen, need not be so refined as the techniques applied by Wooten and Brown (Reference 28). Modification of the nitrogen apparatus to use krypton is slight, and the gas is convenient to handle at room temperature. Also, measurements can be made with relatively small quantities of material.

The technique is especially adapted to measure materials of low specific surface; it may also be applied to small research quantities (20 mg or less) of fairly high-area materials. Therefore, a single volumetric adsorption apparatus may be designed to operate effectively over the region from very-low to very-high areas ( $200 \text{ cm}^2/\text{g}$  to  $2000 \text{ m}^2/\text{g}$ ).

**1.6.1. MODIFICATION OF THE APPARATUS FOR KRYPTON ADSORPTION.** In order to use krypton as well as nitrogen for adsorption measurements, a McLeod gauge, K in Figure 1, and a doser, G, must be included in the apparatus. The McLeod gauge,<sup>5</sup> designed to operate in the desired pressure range (0.1 to 1.5 mm Hg), is calibrated by standard procedures (Reference 32) before it is mounted in the system. The doser is constructed and used in conjunction with manometer C for measuring quantities of krypton added. The doser consists of two 3-way oblique-bore stopcocks connected by a 10-mm o.d. tube and a 2-mm capillary of such length as to produce volumes between stopcocks of approximately 1.8 and 0.6 cc respectively. The volumes of the two tubes are accurately determined by weighing the mercury in the tubes at constant temperature. The procedure is similar to that used in calibrating the nitrogen-system burettes. Doser factors for the two tubes are then calculated from Equation 10. A final check of the vacuum "tightness" of the glassware should be made before measurements are attempted (Section 1.4).

One other volume must be known before the apparatus is ready for use. This is the volume of the McLeod gauge, the lines to stopcock 6a, and the line through stopcock 7a to stopcock 7. This volume is measured by applying the simple P, V relationship described above (Equation 8). First the nitrogen and krypton systems are evacuated by use of the diffusion pump. Stopcocks 3, 4, 4a, 6a, and 7a are then closed. Helium is introduced into burette B (4B level) through stopcock 4 until manometer C registers a pressure of about 500 mm Hg. Stopcock 7 is then closed. At this point the doser contains a quantity of helium at a known pressure and volume. Stopcock 7a is then opened, and the gas is permitted to expand into the McLeod gauge. The

<sup>5</sup>An excellent McLeod gauge is produced by the Todd Scientific Co., Cedars, Pa.

pressure of the new volume is then determined with the McLeod gauge, and the volume of the McLeod system is calculated. This procedure may be repeated and an average value computed from which a "bulb" factor is calculated. All parts of the krypton system are now calibrated, and the system is ready to operate.

1.6.2. SELECTION OF THE SAMPLE SIZE. The choice of sample size is more difficult with krypton adsorption than with nitrogen adsorption because of the rather small quantities of gas adsorbed and the small value of  $P_0$ . For materials having an estimated specific surface of less than  $1 \text{ m}^2/\text{g}$ , samples of approximately 3 to 5 grams should be used with initial doses of krypton of approximately 0.03 cc S.T.P. in a system having a total operating volume of about 175 cc.

1.6.3. REMOVAL OF ADSORBED VAPORS AND THE DEAD-SPACE FACTOR. The conditions governing bake-out, described in Section 1.5.2, apply to materials suitable for krypton adsorption.

The dead-space factor is determined in the same way as for nitrogen areas (Section 1.5.3). In fact, the procedure for using krypton to determine area is identical with the nitrogen procedure up to the point of actual adsorption.

1.6.4. MEASUREMENT OF THE ISOTHERM. Assume that a reasonable amount of sample has been chosen and degassed, the dead-space factor is known, and the system is under high vacuum. Since the adsorption capacity of the sample in question is unknown, several additions of krypton may be needed before equilibrium pressures in the desired range are attained. Before each addition, the krypton already in the doser must be known. At very low pressures (0.05 mm or less) this correction need not be made.

At the beginning of a measurement, stopcocks 7a, 6a, 4a, and 3 are closed. The mercury in burette B is adjusted to the 3B level. Krypton is admitted to the doser and burette system through 4a until a pressure reading of about 50 mm has been established on manometer C. The doser now contains a quantity of gas of known volume at pressure P, as read on the manometer C. Next stopcock 7 is closed, stopcock 7a is opened, and the gas is expanded into the McLeod gauge unit. A pressure reading is recorded, and the quantity of gas that was taken is easily verified by using Equation 9. With the liquid-nitrogen bath in place around the sample tube, stopcock 6a is opened to the McLeod gauge and adsorption begins.

Assume further that the correct amount of krypton has been added and that an equilibrium pressure of about 0.2 mm is established. The reading on McLeod gauge is recorded. The tem-

perature of the doser and McLeod gauge ( $T_B$ ) and the vapor pressure ( $P_0$ ) of the nitrogen in the nitrogen thermometer are recorded. The McLeod gauge is set at its cut-off point, stopcock 7a is closed, and stopcock 7 is opened. The mercury in the burettes is lowered so that manometer C registers a pressure of 10 to 20 mm. This pressure is recorded, along with the temperature of the doser. Stopcock 7 is closed, 7a is opened, and the krypton is allowed to reach a new adsorption equilibrium pressure. When equilibrium is again established, the pressure P, the temperature  $T_B$ , and the pressure  $P_0$  of the nitrogen thermometer are again recorded.

This procedure is repeated until the desired number of sets of data have been obtained. Data for a typical determination are tabulated in Table V. Only the free-space-factor data are given, since the calculations for the free-space factor are similar to those already described.

1.6.5. THE CALCULATIONS. Basically the calculations for determining areas by krypton adsorption are similar to the calculations for nitrogen. They do, however, differ in several respects. First, the total volume of krypton,  $V_t$ , at any equilibrium pressure is the sum of all the krypton additions made previously. The volume adsorbed,  $V_a$ , is obtained by subtracting the

TABLE V. DATA FOR KRYPTON ADSORPTION\*

Line	Gas	Burette or McLeod	Stopcocks			Manometer C Pressure (mm Hg)	McLeod P (mm Hg)	$P_c$ (mm Hg)	$T_B$ ( $^{\circ}C$ )	$N_2, P_0$ (mm Hg)
			6	7a	7					
1	He	3B	closed			184.5			23.3	
2	He	2B	closed			324.3			23.3	
3	He	2B	open			240.8		239.7	23.4	
4	He	3B	open			154.0		153.3	23.4	
5	Kr	cut-off	closed	closed	open	27.9			23.3	
6	Kr		closed	open	closed		0.300		23.3	
7	Kr		open	open	closed		0.170	0.169	24.2	809.5
8	Kr	cut-off	open	closed	open	16.3			24.2	
9	Kr		open	open	closed		0.300	0.299	24.3	809.5
10	Kr	cut-off	open	closed	open	16.1			24.3	
11	Kr		open	open	closed		0.435	0.433	24.4	809.5

\*Sample weight = 2.5145 grams.

volume of gas in the McLeod system,  $V_{mc}$ , and the volume of gas  $V_s$  in the free space surrounding the sample and not adsorbed,  $V_s$ , from the total volume of krypton present.

$$V_a = V_t - V_{mc} - V_s \tag{13}$$

$V_t$  and  $V_{mc}$  are calculated from Equation 9, and  $V_s$  is calculated from

$$V_s = (P_c) (F_s) \tag{14}$$

The correction for the deviation of krypton from ideality is omitted, since small quantities and low pressures are being employed.

Second, the value of  $P_0$  for krypton is obtained indirectly. Figure 10 shows an extrapolated plot of  $\log P$  of liquid Kr versus  $1/T$  (References 33 and 34), superimposed on a plot of  $\log P$

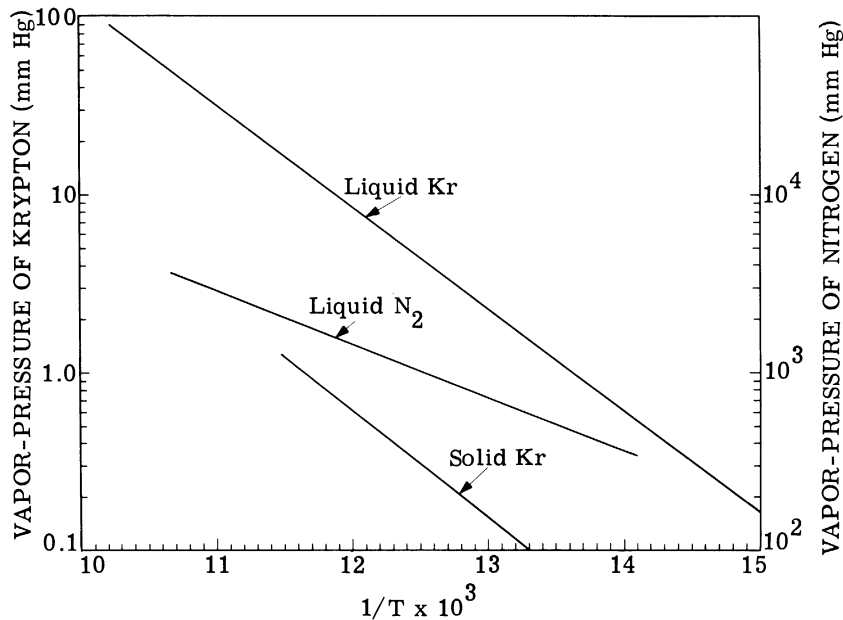


FIGURE 10. VAPOR PRESSURE OF LIQUID NITROGEN, LIQUID KRYPTON, AND SOLID KRYPTON AS A FUNCTION OF TEMPERATURE

of nitrogen versus  $1/T$  (Reference 35) over the temperature range  $70^{\circ}\text{K}$  to  $85^{\circ}\text{K}$ . To determine the  $P_0$  for liquid krypton, the value of  $1/T$  for  $P_0$  nitrogen is determined, and a vertical is then drawn to intersect the  $\log P$  versus  $1/T$  curve for liquid krypton. The intersection represents the  $P_0$  of liquid krypton at the operating temperatures.

If the krypton apparatus alone has been constructed, the value for  $P_0$  can be determined by noting the vapor pressure of solid krypton. This is done at the end of the surface area measure-



ment by admitting an excess of krypton gas to the sample and measuring the equilibrium vapor pressure of the solid with the McLeod gauge. From this, the value of the vapor pressure of the supercooled liquid is graphically obtained from Figure 10. Some error is introduced by this technique, since changes in  $P_0$  due to bath temperature changes during a determination must be absorbed in the final measured  $P_0$  of the solid. However, the error is small.

The lines in Column A of Table V are listed as in Column A of Table VI. The other columns in Table V are as follows.

- B Gas
- C Burette bulb, or position of McLeod gauge
- D, E, F Positions of stopcocks
- G Pressure reading at manometer C when krypton is being added to doser
- H Pressure at adsorption equilibrium
- J Correct pressure
- K Temperature of bulbs
- L Pressure reading at manometer I

Here again the lines (Column A) of the data of Table V correspond to the lines (Column A) of the calculations in Table VI. The gas being used is represented in Column B of Table V, the burette bulb being used, or the position of the McLeod gauge, in Column C; the positions of the primary stopcocks are represented in Columns D, E, and F, the pressure of manometer C when making krypton additions to doser, G, in Column G, the pressure at adsorption equilibrium in Column H, and the corrected pressure in Column J. In Column K the temperature of the bulbs is recorded and the pressure reading of manometer I in Column L.

TABLE VI. WORK SHEET FOR CALCULATING B.E.T. VARIABLES FROM DATA IN TABLE V

A	B	C	D	E	F	G	H	J	K	L
Line	Gas in Doser (cc)	$V_t$ (cc)	$V_{mc}$ (cc)	$V_s$ (cc)	$V_a$ (cc)	Krypton $P_0$ (mm Hg)	$P/P_0$	$1 - P/P_0$	$V_a(1 - P/P_0)$	$P/V_a(P_0 - P)$
	Free space factor calculated as before = 0.0140 cc/mm.									
5	0.0600	0.0600								
7	0.0004	0.0600	0.0336	0.0024	0.0240	2.79	0.0609	0.9391	0.0226	2.70
8	0.0349	0.0945								
9	0.0006	0.0945	0.0592	0.0042	0.0311	2.79	0.1075	0.8925	0.0278	3.87
10	0.0345	0.1284								
11		0.1284	0.0858	0.0061	0.0365	2.79	0.1559	0.8441	0.0308	5.06

Column B of Table VI represents various quantities of krypton in the doser under different conditions. Since the adsorption apparatus is evacuated at the beginning of a determination, no correction for the gas remaining in the doser is needed before the first addition of krypton. However, correction is needed for successive additions. Line 5 (Table V and Table VI) represents the data and calculations for the first addition. However, the second addition, as represented in lines 7 and 8 of both tables, needs correction. Line 7, Column B, of Table VI gives the volume of krypton in the doser under the conditions of line 7, Table V, i.e., at the first equilibrium pressure; and line 8, Column B of Table VI gives the volume of krypton in the doser under the conditions of line 8 of Table V, i.e., after the second addition of krypton. The actual volume of krypton added to the krypton system, then, is line 8, Column B of Table VI, minus line 7, Column B of Table VI. Adding this volume to that given in line 5, Column C of Table VI, gives the true total volume of krypton present in the system at the end of the second addition. This procedure is repeated for other additions. Columns D, E, and F are as before; Column G has already been described; Column H is calculated by dividing Column H of Table V by Column G of Table VI.

Here again, the values in Column L of Table VI versus those in Column H of Table VI can be plotted linearly. From the slope and intercept of the plot,  $V_m$  can be calculated. The area is computed from Equation 5.

The B.E.T. variables, as determined from the data and calculations of Tables V and VI, are plotted in Figure 11.  $V_m$ , calculated from Equation 4, is 0.0385 cc; the area computed from this figure is 807  $\text{cm}^2/\text{gram}$ .

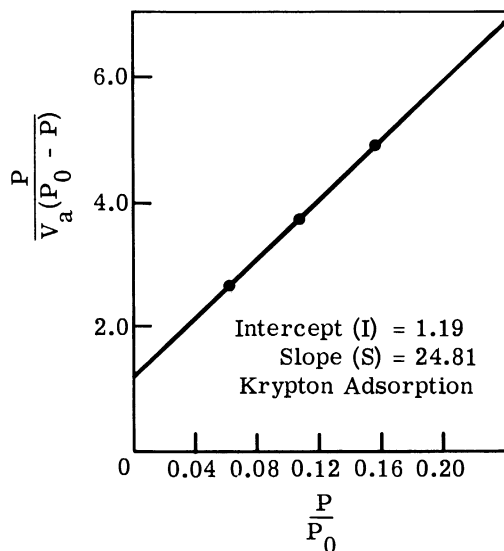


FIGURE 11. PLOT OF B.E.T. VARIABLES FOR DATA IN TABLE VI

1.6.6. ALTERNATIVE METHOD. An alternative method of determining the data has been described by Beebe et al. (Reference 30) and by Bloecher (Reference 31). This technique uses the fact that the McLeod gauge can serve as a burette. Consequently, various known quantities of krypton can be removed in order to determine  $V_a$ . This is a desorption process.

### 1.7. MEASUREMENT OF PORE VOLUME DISTRIBUTION

The quantity of gas adsorbed by a finely divided solid is essentially the sum of the gas held on the geometric surface of the particle and the gas as condensate within the pores of the sorbent. (With many solid adsorbents this latter contribution to adsorption is very large.) For many purposes, the change in surface area is used to determine the effect of various treatments on the structure of solid adsorbents. However, a more informative result can be obtained by noting a change in the pore volume distribution of a porous solid.

The measurement of pore volume distribution from nitrogen isotherms has been described by Barrett et al. (Reference 14). Barrett's method is useful with materials having pore radii within the range 5 Å to 300 Å. Above 300 Å the mercury porosimeter technique described by Ritter and Drake (Reference 36) is applicable. These two techniques have been found to augment each other (Reference 37).

The calculation of pore volume distribution requires data from a nitrogen isotherm, which can be collected by use of the gas adsorption apparatus. The technique is not basically different from that used to determine  $V_m$  from nitrogen adsorption isotherms.

An example of the calculations is given by Barrett; however, the data taken and their general use will be briefly explained here.

Three points on the nitrogen isotherm were used to determine  $V_m$ ; as many as twenty or thirty points will be needed to construct the complete isotherm necessary for computing pore volume distribution. Table III may be used to record the data, and Table IV, excluding Columns F, G, H, and J, may be used as a work sheet. The adsorption branch and the desorption branch of a nitrogen isotherm are constructed by determining the volume of nitrogen adsorbed per gram of adsorbent ( $V_a$ /gram) at various relative pressures from 0.05 to near 1.0 and then from 1.0 to 0.05. A typical isotherm is shown in Figure 12. From the Kelvin equation (Equation 7), a master work sheet may be set up giving calculated values of the relative pressure for given values of pore radius. From the desorption branch of the isotherm in Figure 12, one can tabulate the volume of nitrogen adsorbed per gram at the calculated relative pressures corresponding to a particular pore radius. These volumes of gas are then converted to liquid volumes. Some idea of the probable pore volume distribution can be obtained by constructing a plot of the difference

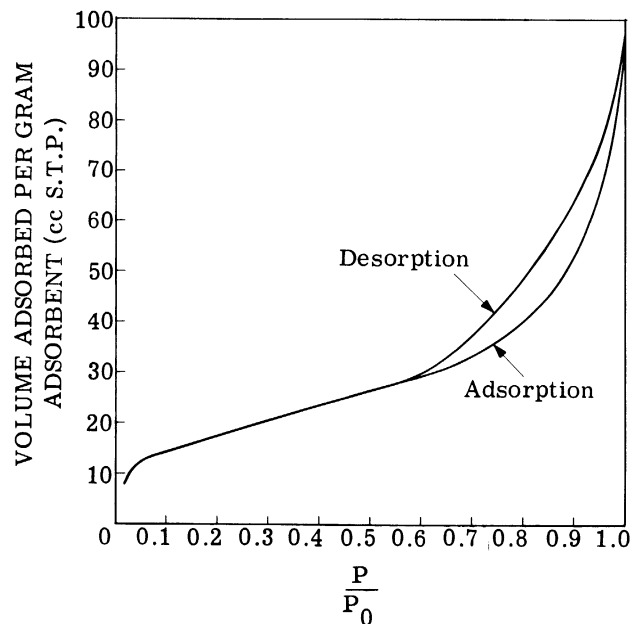


FIGURE 12. TYPICAL NITROGEN ISOTHERM FOR USE IN CALCULATING PORE VOLUME DISTRIBUTION

between the liquid volumes,  $\Delta V_1$ , divided by the pore radius increment chosen,  $\Delta r$ , versus the average pore radius of the increment,  $\bar{r}$ .

Barrett incorporated a correction for a change in pore volume over a given increment in pore radius. This correction, discussed in detail in Reference 14, provides a method whereby  $\Delta V_1$  is modified to take into account the differences in pore radius caused by physically adsorbed gas and pore condensate.

Upon completion of the correction for the liquid volume in the pores, several informative plots may be constructed. From the data thus calculated a plot of pore radius,  $r$ , versus the total pore volume in pores of radius equal to or larger than  $r$  can be made. An example is shown in Figure 13. From the smoothed curve, approximate pore volume maxima can be found by noting the portions of the curve where the slope is changing most rapidly.

Plotting the derivative of the curve in Figure 13 versus the average pore radius gives a distribution curve describing the relative contributions of the various pore sizes to the total pore volume. The derivative is obtained by dividing the value of  $\Sigma V_p$  at  $\bar{r}$  (from Figure 13) by the particular pore radius increment that determined  $\bar{r}$ , i.e.,  $(\Sigma V_p / \Delta r)_{\bar{r}}$ , and plotting this against  $\bar{r}$ . Such a plot, illustrated in Figure 14, shows changes in the pore radius which account for large changes in pore volume.

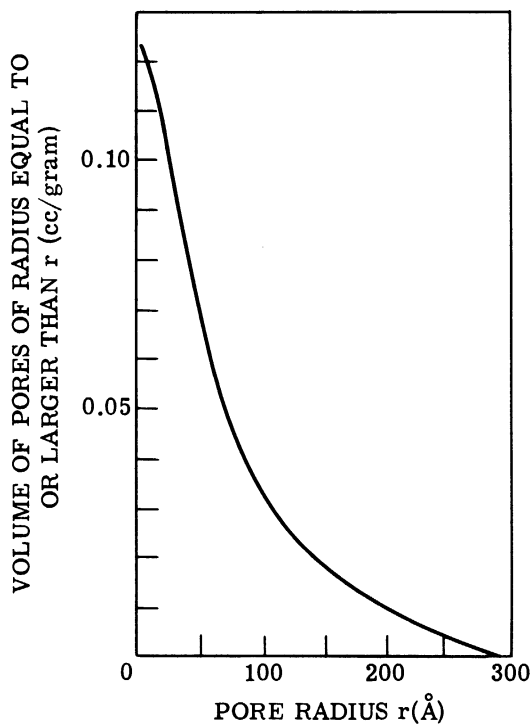


FIGURE 13. VOLUME OF PORES OF RADIUS EQUAL TO OR LARGER THAN  $r$ , PLOTTED WITH RESPECT TO PORE RADIUS

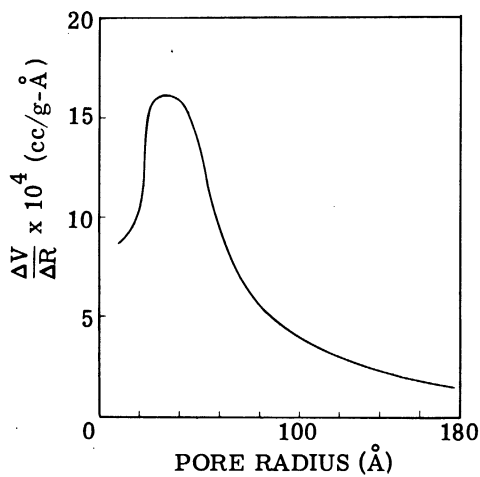


FIGURE 14. PLOT OF THE PORE VOLUME DISTRIBUTION AS A FUNCTION OF THE PORE RADIUS

## 1.8. DETERMINATION OF THE DENSITY OF SOLID MATERIALS BY HELIUM DISPLACEMENT

The helium displacement technique may be used to determine the densities of finely divided solids. These are true densities if vapor pockets are assumed absent. Helium has several properties which make it ideal for density measurements: it is chemically inert; it does not adsorb on most materials at room temperature; it can penetrate into pores not accessible to other displacing fluids such as toluene or benzene; and it is virtually ideal in its behavior as a gas.

**1.8.1. CHOICE OF SAMPLE SIZE AND SAMPLE TUBE.** A sample tube large enough to accommodate 50 cc of the sample is recommended. When smaller volumes are used there is risk of losing significant figures in the calculations. Sample tube D, shown in Figure 2, has been found convenient for the measurement. The standard joint must be modified slightly for materials of fairly large particle size; a standard taper adaptor is then used.

**1.8.2. SAMPLE TUBE CALIBRATION.** The density system consists of the sample tube, the line to each of the burettes at the desired bulb volume, and the line to the zero marker of the manometer. First the volume of the empty sample tube is determined; four or five separate determinations are enough. The average value obtained, when used in the calculations, reduces the errors caused by different methods of seating the standard taper joints.

The system is first evacuated with a diffusion pump. After degassing, the sample tube is immersed in a 600-ml beaker of water at room temperature, or a constant-temperature bath. Stopcock 6 is closed. Helium is introduced into the burette system through stopcock 4 until there is a pressure difference of about 150 mm Hg at 4B bulb level. The pressure  $P_1$  and temperature are recorded. Stopcock 6 is then opened and a few minutes are allowed for equilibrium to be established. The manometer is again adjusted to the zero marker, and the new pressure,  $P_2$ , is recorded. The volume of the sample tube is determined from Equation 15, which is similar to Equation 8.

$$P_1 V_1 = P_2 V_2 = P_2 (V_1 + V_c)$$

or

$$V_c = V_1 (P_1 - P_2) / P_2 \quad (15)$$

Where subscripts 1 and 2 denote stopcock 6 closed and open, respectively;  $V_1$  is the total calibrated volume of the burette system up to stopcock 6; and  $V_c$  is the calibrated volume of the empty sample tube. This procedure may be repeated and the average value taken as the correct calibrated volume.

1.8.3. PREPARATION OF SAMPLE. A sample is introduced into the sample tube, the tube is seated into the 10/30 standard taper joint, and the sample is degassed, with the precautions previously mentioned. (A separate high-vacuum degassing unit with suitable traps should be provided if organic materials are present that are volatile at 200°C.) Then the oven is removed, and the sample and tube are cooled and immersed in a liquid at constant temperature.

1.8.4. DENSITY DETERMINATION. The procedure is similar to that used in the calibration. Stopcock 6 is closed and helium is introduced into the burette system through stopcock 4 until a pressure of 200 mm Hg is reached at 4B bulb level. The system is equilibrated thermally and the pressure,  $P_1$ , recorded. Stopcock 6 is then opened, the system is again permitted to attain equilibrium, and the new pressure is recorded.

A development of the density relationship follows. Constant temperature is again assumed. It follows from Equation 15 that when stopcock 6 is closed, then opened,

$$P_1 V_1 = P_3 V_3 = P_3 [V_1 + (V_c - V_{sd})] \quad (16)$$

where  $P_1$ ,  $V_1$ , and  $V_c$  are as before;  $V_{sd}$  is the volume of the solid present in the sample tube; and  $P_3$  is the pressure with stopcock 6 open and a sample present. Solving for  $V_{sd}$ ,

$$\begin{aligned} P_3 V_{sd} &= P_3 V_1 + P_3 V_c - P_1 V_1 \\ V_{sd} &= V_1 + V_c - V_1 (P_1/P_3) \\ V_{sd} &= K - k(P_1/P_3) \end{aligned} \quad (17)$$

where  $K = V_1 + V_c$  and  $k = V_1$ .  $K$  and  $k$  are constants only when pressures measured at the same bulb volume are compared. The density is calculated by dividing the weight of sample taken by  $V_{sd}$ , i.e.,

$$D = \text{Sample Wt}/V_{sd} \quad (18)$$

Several checks of  $V_{sd}$  can be made by taking the pressure reading of various bulb volumes before and after stopcock 6 has been opened. By correlating these pressures according to bulb number, several checks can be made with one sample of helium.

1.8.5. CALCULATIONS. Tables VII and VIII represent data and calculations for a typical density determination. The columns in Table VII are arranged as follows.

- B Position of the mercury in the burettes
- C Position of stopcock 6

TABLE VII. DATA FOR DENSITY DETERMINATIONS OF SOLIDS\*

A	B	C	D	E	F	G
Line	Bulb	Stopcock 6	P <sub>obs</sub> (mm Hg)	Sample Temperature (°C)	V <sub>1</sub> (k) (cc)	K (cc)
			(Calibration)			
1	4B	closed	178.5	25.0	106.57	
2	3B	closed	327.3	25.0	58.17	
3	2B	closed	575.8	25.0	33.09	
4	2B	open	225.8	25.1		
5	3B	open	173.5	25.1		
6	4B	open	120.3	25.1		
			(density)			
7	4B	closed	241.3	23.0	106.57	158.13
8	3B	closed	442.5	23.0	58.17	109.73
9	2B	closed	778.5	23.0	33.09	84.65
10	2B	open	390.1	23.0		
11	3B	open	282.5	23.0		
12	4B	open	184.3	23.0		

\* Sample weight = 77.052 grams.

TABLE VIII. WORK SHEET FOR DENSITY DETERMINATIONS OF SOLIDS

(Calibration—Equation 15)

$$\text{lines 1 and 6} \quad V_c = \frac{106.57(178.5 - 120.3)}{120.3} = 51.56 \text{ cc}$$

$$\text{lines 2 and 5} \quad V_c = \frac{58.17(327.3 - 173.5)}{173.7} = 51.57 \text{ cc}$$

$$\text{lines 3 and 4} \quad V_c = \frac{33.09(575.8 - 225.1)}{225.1} = 51.55 \text{ cc}$$

Average value of  $V_c$  is 51.56 cc.

(Density—Equation 18)

$$\text{lines 7 and 12} \quad D = \frac{77.052}{158.13 - 106.57(241.3/184.3)} = 4.143 \text{ g/cc}$$

$$\text{lines 8 and 11} \quad D = \frac{77.052}{109.73 - 58.17(442.5/282.5)} = 4.140 \text{ g/cc}$$

$$\text{lines 9 and 10} \quad D = \frac{77.052}{84.65 - 33.09(778.5/390.1)} = 4.138 \text{ g/cc}$$

Average value of  $D$  is 4.140 g/cc.



- D Observed equilibrium pressure
- E Sample temperature
- F Accumulative bulb volume corresponding specifically to the burette bulb being used
- G Accumulative bulb volume plus the volume of the calibrated empty sample tube corresponding to the particular burette bulb in use

Table VII shows the calculations for an empty-tube calibration and a density determination. It is estimated that the density values are reproducible to within  $\pm 2$  units in the second decimal place.

## 2

### GRAVIMETRIC APPARATUS FOR THE MEASUREMENT OF THE SORPTION OF GASES IN AND ON SOLIDS

#### 2.1. INTRODUCTION

Although the adsorption apparatus described in Section 1 is versatile, it cannot be applied to all types of adsorption experiments. To supplement the measurements of a volumetric adsorption system, it is advantageous to have access to a gravimetric adsorption system. A particularly important advantage of a gravimetric apparatus is that one can make continuous measurements of extremely small changes in a chemical system. But as happens with all refinements, the increased sensitivity of the measurement is accompanied by many problems not encountered in the volumetric system. The use of some balances at times becomes very tedious and the time required for perfecting the operation of the balance for different techniques can be relatively long.

Several types of "balances" are used in gravimetric work. The quartz-spring type used by some authors (Reference 38) depends on the fact that the elongation of a quartz helix is proportional to the mass acting on the spring. Thus the quantity of gas adsorbed, for example, can be weighed. Automation of this type of balance is discussed by Klevens et al. (Reference 39).

The torsion balance, which was used by Donau (References 40 and 41) among others, is a beam balance with fixed supports. Here the mass rotates the beam over a stationary quartz rod; the deflection of a reference needle is a measure of the mass change.

Another design is the cantilever balance (Reference 42). This design operates on the principle that a horizontally fixed, fused silica rod will bend along its length in proportion to a force applied some distance along the rod.<sup>6</sup>

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<sup>6</sup>Variations of the above-mentioned balances may be purchased from the Microchemical Specialties Co. of Berkeley, California.

A fourth type of balance, which will be discussed here, is the quartz beam microbalance. It is the balance discussed by Czanderna and Honig (References 43, 44, and 45) and has been used by the author (Reference 46). This balance has several advantages, which will be summarized later. The design was automated by Cochran (Reference 47); refinements of his automation scheme have also been described (Reference 48). Rhodin (Reference 49) gives an excellent general discussion of balances, and Gulbransen (Reference 50) discusses their application.

## 2.2. CONSTRUCTION OF THE BALANCE SYSTEM

**2.2.1. THE MICROBALANCE.** The balance illustrated in Figure 15 consists of a symmetrical beam (A), constructed from fused silica rod one millimeter in diameter; a carriage (B) designed to support the beam is constructed from fused silica rod two millimeters in diameter. Fused silica was chosen because of its strength, chemical inertness, and small temperature coefficient of expansion. A scale drawing of the balance is shown in Figure 16.

The balance beam is supported on two pivot points made of tungsten wire 0.005 inch in diameter. Before being installed on the beam, the wires are electropolished to a point by being dipped into and out of a 20% sodium hydroxide solution while passing an alternating current of 6 to 10 volts (higher voltages cause imperfect polishing). Special care should be taken to avoid annealing the hard-drawn wires, for annealed tungsten points become blunted after several months of operation and must be replaced. Once properly prepared, the wires are cemented to the beam with fused silver chloride.

A variation of this method may also be used to prepare the tips. Unpolished tungsten wires are cemented in place on the beam, and then the beam is placed in a horizontal position with the wires dipping into the basic solution. As the tips become polished they are reduced to the same length. In the first method the tips are dipped into and out of the solution by a rotating cam device; in the second the beam may be rocked by hand. Whichever method is used, the tips are inspected through a low-power microscope and those found imperfect or split are discarded or repolished.

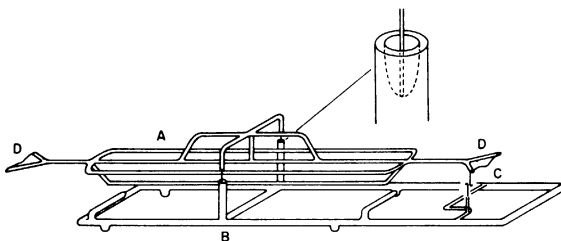


FIGURE 15. THE QUARTZ BEAM MICRO-BALANCE

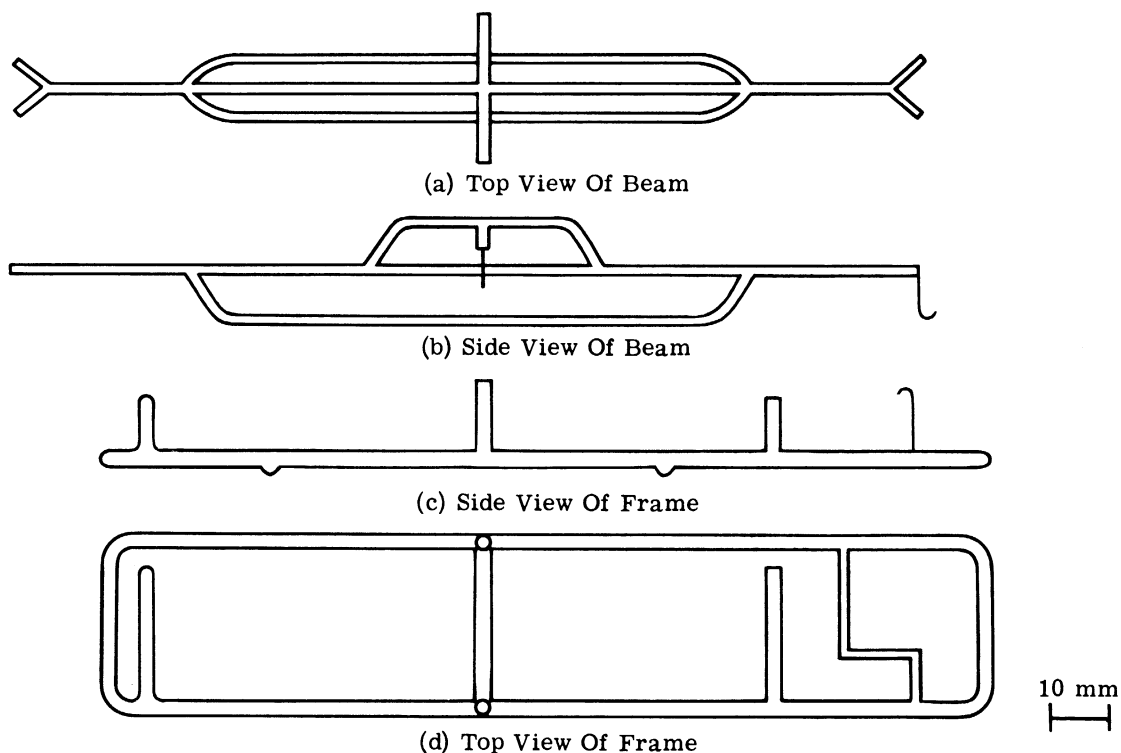


FIGURE 16. SCALE DRAWING OF THE MICROBALANCE

The pivot support wires of the beam rest in cups resembling parabolic cones and located in the ends of vertical silica rods attached to the carriage. The cups are prepared by the use of a simple glassblowing technique that has been described by Johnson and Nash (Reference 51).

One indicator hook (C) is attached to the beam and one to the carriage. These hooks are located in the same vertical plane and are observed by means of a Gaertner 38X cathetometer telescope when the balance is in use. They are fashioned from quartz fiber. The null system was recently modified (Reference 52) to use two horizontally opposed tungsten wires (3-mil) instead of quartz hooks. The wires are pointed, and aligned so that they almost touch. The use of tungsten wires minimizes interfering light reflections; if the points are properly aligned at null position, the necessity of an expensive traveling microscope is eliminated.

Y branches (D) are located in a horizontal plane at the ends of the beam. Across the branches of each Y, a tungsten wire two mils in diameter is cemented with fused silver chloride. A slight depression is made in the center of each wire. These cross members can also be formed from fused quartz (Reference 48).

2.2.2. **THE SUPPORT FIBERS.** Thin fibers are used to suspend objects from the balance beam at the Y branches mentioned above. They are drawn from fused silica rods, and hooks are fashioned at their ends. It is important that they be as thin and uniform as possible (Reference 53). If they are not uniform in diameter, they will bend when they cool. They can be straightened by suspending a platinum weight from the lower hook on the fiber and carefully annealing the entire length of the fiber with the flame of a microtorch.

2.2.3. **THE SAMPLE CONTAINER.** Spherical sample bulbs, approximately 10 mm in diameter, are constructed from fused silica (or Pyrex). A hook is fashioned from the surface of the bulb, and the strain is relieved in the manner described in the preceding paragraph. A tiny hole (0.5 to 3 mm diameter) is formed in the top of the bulb so that the bulb can be filled with a powdered sample (up to 1 gram) and gases can be admitted.

2.2.4. **THE ALNICO WIRE NEEDLE.** An Alnico wire needle employed for magnetic compensation (see below) is encased in a Pyrex tube, and a hook is fashioned at each end. It is important that the needle remain motionless within the glass, that the unit be as light as possible, and that the encasement be vacuum tight. The needle is approximately three inches long and about 1/16 inch in diameter. It is magnetized by brushing a small horseshoe magnet (always in the same direction) two or three times over its length.

### 2.3. ASSEMBLY OF THE BALANCE

In operation, the balance beam and the support frame are aligned and enclosed in a Pyrex envelope, as shown in Figure 17. For best operation the tungsten points should be in the same horizontal plane and the beam should be horizontal at the null position. The carriage is held in place with a drop of Apiezon-W black wax applied inside the housing to two legs of the frame. Fused silica fibers (C) are suspended from the Y branch supports; the platinum weights (A), Alnico needle (B), sample bulb (D), and its counterbalance (E) are suspended on other fibers. The curvature of each fiber hook in the train should contain a well defined minimum. A fused silica tube (25-mm o.d.) is mounted around each fiber train via a 29/42 standard taper ground-glass joint. The flat-ground end-caps of the balance housing and the fused silica legs are cemented with Apiezon-W wax. One housing cap is designed to be attached to the auxiliary vacuum rack. Two Hevi Duty<sup>7</sup> type 70 tube furnaces are used to heat the sample and the counterweight.

The balance must be installed with extreme care to assure that the parabolic cups and the tungsten tips are free from grease and small pieces of grit. The entire balance and the housing

<sup>7</sup> Manufactured by the Hevi Duty Electric Company, Milwaukee, Wis.

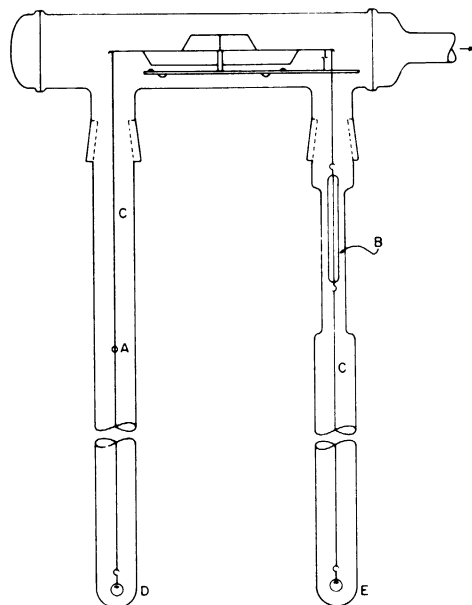


FIGURE 17. THE MICROBALANCE ASSEMBLY

must first be cleaned with soap and water, rinsed with acetone, allowed to dry, and gently flamed with a microtorch.

**2.3.1. THE AUXILIARY VACUUM LINE.** The basic components of the vacuum line, such as fore pump, diffusion pump, traps, gas storage vessels, manometers, etc., were discussed in Section 1.3. (The usual precautions should be taken.) Figure 18 shows the auxiliary system used with this particular balance. It is recommended that stopcocks be equal in quality to the E & K precision-grade, bulb types. Most of the stopcocks used were either 2- or 4-mm oblique-bore units.

**2.3.2. GENERATION OF GASES.** The acquisition of the gases to be used in the experiments is extremely important. In the volumetric experiments, pure gases are obtained by removing impurities from gases available commercially in tank cylinders. It is also convenient to obtain small amounts of high-purity gases by the thermal decomposition of appropriate solid compounds. For example, oxygen and nitrogen may be obtained from the thermal decomposition of  $\text{KMnO}_4$  and  $\text{NaN}_3$ , respectively. To accomplish this in the laboratory, a 500-ml round-bottom flask (Figure 18) is half filled with either  $\text{KMnO}_4$  (for oxygen generation) or about 10 grams of  $\text{NaN}_3$  (for nitrogen generation), and sealed into a purification train. A Glasscol heating mantle is attached to each flask, and a copper gauze tube lined with asbestos paper is fitted around the as-

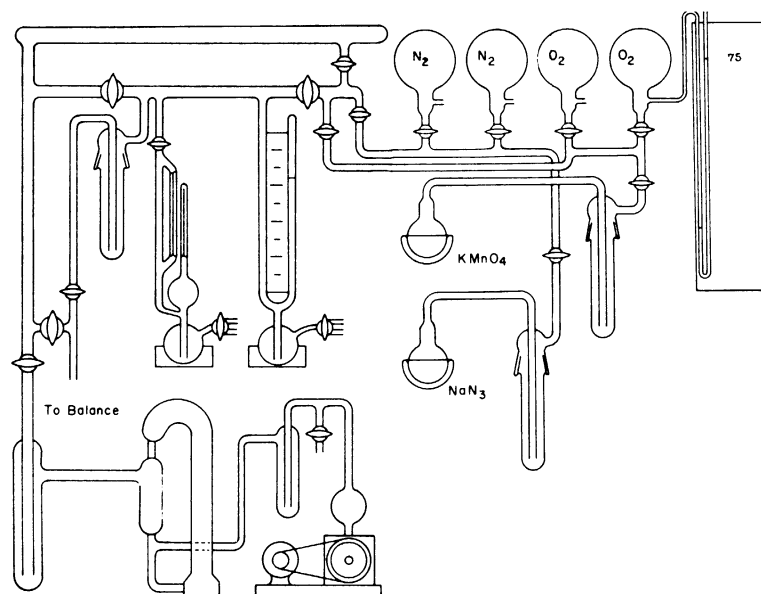


FIGURE 18. THE AUXILIARY VACUUM SYSTEM

sembly. The solid can then be heated in vacuo from room temperature.  $\text{KMnO}_4$  can be heated to  $200^\circ\text{C}$ , and  $\text{NaN}_3$  to about  $300^\circ\text{C}$ , before significant decomposition occurs. The decomposition rate is moderate if a heating rate of about  $1^\circ\text{C}$  per minute is maintained. The quantity of  $\text{NaN}_3$  used must be calculated so that the nitrogen generated is compatible with the absolute volume of the gas reservoirs at a pressure between 700 and 900 mm Hg. This precaution is not necessary with  $\text{KMnO}_4$  since the decomposition of this material is easier to control. Extreme caution should be exercised during the decompositions, especially with the  $\text{NaN}_3$ .

The first few millimeters pressure of each gas should be discarded. As the gases are generated, each passes through a trap filled with 4-mm glass beads and cooled with dry ice. If needed, a desiccant such as  $\text{P}_2\text{O}_5$  or  $\text{BaO}$  should be used. The dried gases are collected in three-liter storage flasks; each flask is wrapped with masking tape as a safety measure and is equipped with an open-end mercury manometer which serves to detect leaks and to indicate the quantity of gas in the storage system; closed-end manometers may also be used.

#### 2.4. CONSTRUCTION OF THE FURNACE THERMOCOUPLES

The thermocouples used to measure the temperature of the sample are fashioned from No. 18 Chromel and Alumel wires. The thermocouple junctions are made by use of a medium temperature oxygen-natural gas flame and a sodium borate flux. The lead wires are threaded into a two-hole ceramic rod and cemented with Sauereisen cement into the wall of a type 70 Hevi

Duty tube furnace. Each wire of the Chromel-Alumel junction is silver soldered to copper lead wires; these are the cold junctions which are kept at  $0^{\circ}\text{C}$  during an experiment.

2.4.1. CALIBRATION. Since it is desirable to calibrate the thermocouples in the position in which they are to be used, the following procedure is adopted. A second thermocouple is constructed in the manner described above. The furnace couples are compared with this master couple by means of an experimental arrangement similar to that used for the microbalance assembly. A sample-tube furnace is set aside and the quartz tube of the balance is clamped in position. A quartz thimble filled with a calibration solid is inserted inside the leg. The tip of the master thermocouple is inserted into a 10-mm o.d. quartz sleeve, and the assembly is inserted into the thimble; the position of the tip is adjusted in the furnace to correspond to the sample position on the microbalance.

The temperature of the furnace is increased at intervals and the e.m.f. of the master thermocouple is compared to the furnace thermocouples. A primary calibration of the master thermocouple (in situ) is obtained from the freezing points of the various calibration solids used (Pb, Sn, Zn, Sb, Ag, and NaCl). The furnace thermocouples register higher temperatures than the master couple; this is to be expected, because of radiation losses through the ends of the tube furnace.

In an identical experiment using the counterpoise furnace, the results obtained duplicated the results of the sample thermocouple calibration. Therefore, the data of the sample furnace calibration may be used to describe both furnace thermocouples. The data for a typical calibration are given in Table IX. Sample temperatures can be calculated by use of a plot of the data in Table IX and a Leeds and Northrup conversion table.

## 2.5. OPERATION OF THE BALANCE

The microbalance is used as a null-indicating instrument. A small D-type solenoid (Figure 19) is fitted around the balance leg containing the Alnico needle so that one end of the needle

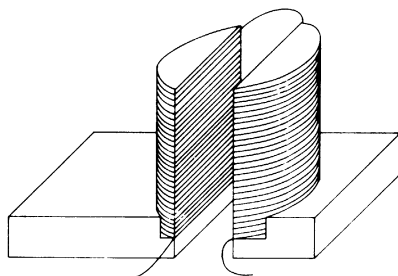


FIGURE 19. THE MAGNETIC COMPENSATION SOLENOID

TABLE IX. FURNACE THERMOCOUPLE CALIBRATION

Furnace Thermocouple (mv)	Master Thermocouple (mv)	Temperature (°C)
0	0	0
11.77	11.11	269
12.70	12.05	293
20.50	19.20	464
21.30	20.19	487
23.00	21.80	525
24.70	23.20	557
27.30	25.80	619
27.91	26.08	625
30.89	29.20	698
31.30	29.20	698
34.55	32.40	772
38.05	35.71	853
39.31	37.10	890
42.16	39.82	960
44.00	41.65	1009

is suspended in the center of the solenoid and the other end is out of the solenoid. Each D is wound with 55 turns of No. 22 insulated copper wire. A small current passing through the magnetic compensation solenoid is used to maintain the balance in null position (Figure 20). The current is provided by three 6-volt lead storage batteries connected in parallel; it is controlled by a resistance box (Helipot, 2-watt; Figure 21). The Alnico needle is permanently magnetized (Section 2.2.4) so that it can be attracted into or repulsed by the field of the solenoid. The change in compensating current through the solenoid is proportional to the change in mass of the sample, as measured with a type-B Rubicon potentiometer by observing the change in voltage across a standard Manganin resistor (Figure 22). It is important that the solenoid remain in place after the balance has been calibrated; otherwise recalibration is necessary.

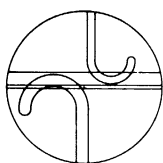


FIGURE 20. STANDARD NULL POSITION

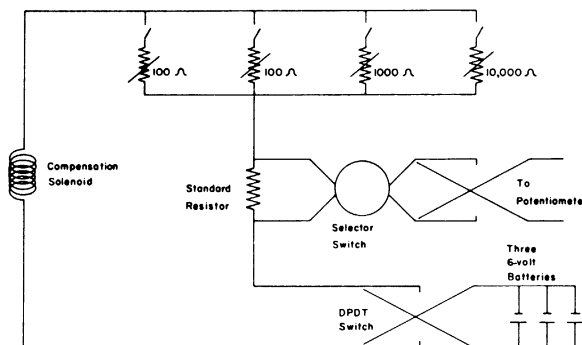


FIGURE 21. THE MICROBALANCE ELECTRICAL CIRCUIT



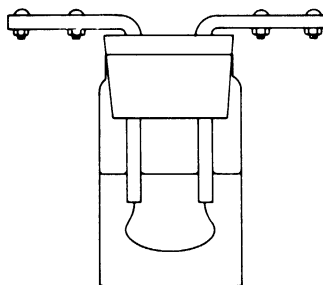


FIGURE 22. STANDARD RESISTOR

## 2.6. CALIBRATION OF THE BALANCE

2.6.1. ABSOLUTE METHOD. A primary method based on Archimedes' principle is best for calibrating the microbalance. If a mass of volume  $V$  is suspended from the microbalance, and the (nitrogen) gas pressure surrounding the mass is varied, the compensation voltage will vary linearly with the pressure at room temperature (but see Section 2.7.2). A plot of these variables will have a slope  $S_n$  that depends on the volume of the mass being measured. If two samples with identical masses and different volumes are chosen, the following relation may be employed to calculate the sensitivity of the balance.

$$S = \frac{(V_1 - V_2)M \cdot 10^6}{(S_1 - S_2) ZPV} \quad (19)$$

where  $S$  is the balance sensitivity micrograms/microvolt;  $M$  is the molecular weight of the gas (nitrogen, 28.016 grams/mole);  $V_1$  is the volume of a sealed Pyrex bulb (milliliters), and  $V_2$  is the volume of an equivalent mass of platinum wire.  $S_1$  and  $S_2$  are the calculated slopes (microvolts/millimeter) of the curves obtained from a plot of compensation voltage versus (nitrogen) gas pressure for each volume;  $P$  is 760 mm;  $V$  is 22,400 ml, and  $Z$  is a constant (equal to 1.0915 at room temperature) which is used to correct the  $PV$  product for the nonideality of nitrogen.

In practice, a sealed Pyrex bulb approximately 1 cm in diameter is used for  $V_1$ . A hook is fashioned from the surface of the bulb. The volume of the bulb may be determined in several ways. The easiest method is to weigh the bulb first in air and then in distilled water. Since it will float in water, an appropriate weight of Pt must be added to submerge it. Care should be taken to avoid trapping bubbles on the bulb and the Pt weights. The difference in mass between the two weighings is equal to the mass of water displaced by the bulb. The volume of water displaced is calculated by dividing the difference in mass by the density of water at the temperature

of the weighing. The bulb is then attached to the fiber train at A (Figure 17), and pressure-compensation voltage data are recorded.

$V_2$  is much easier to obtain. A mass (in air) of Pt wire equal to the mass of the bulb ( $V_1$ ) must be procured. The volume of the Pt wire is obtained by dividing the mass of the wire by the density of Pt (21.45 grams/ml). The Pt wire is then attached to the fiber train in place of the buoyancy bulb, and a set of pressure-compensation voltage data is recorded. It is important that no change in the suspension fibers or counterweights be made other than to remove the Pyrex bulb and replace it with the platinum weight. The masses for  $V_1$  and  $V_2$  should not be different by more than one milligram.

Typical data are given in Table X and represented graphically in Figure 23. The sensitivity of the balance is calculated from Equation 19.

TABLE X. MICROBALANCE CALIBRATION DATA

Volume $V_1$ *		Volume $V_2$ **	
Nitrogen Pressure (mm Hg)	Compensation e.m.f. (mv)	Nitrogen Pressure (mm Hg)	Compensation e.m.f. (mv)
6.9	19.866	4.2	20.874
28.7	19.455	72.8	20.720
74.9	18.598	117.0	20.614
105.1	18.050	176.7	20.485
149.7	17.237	253.4	20.320
181.1	16.648	317.3	20.194
219.3	15.941		
263.1	15.142		
297.6	14.497		
337.4	13.764		
336.6	13.742		
296.7	14.481		
194.8	16.384		
97.4	18.192		
4.3	19.916		

\*  $V_1 = 0.545_3$  ml.

\*\*  $V_2 = 0.0112$  ml.

2.6.2. INTERNAL METHOD. A second method of calculating the sensitivity of the balance is to use an internal standard. By measuring known mass changes as e.m.f. changes, the sensitivity factor can be calculated. This procedure is satisfactory and convenient. The reference

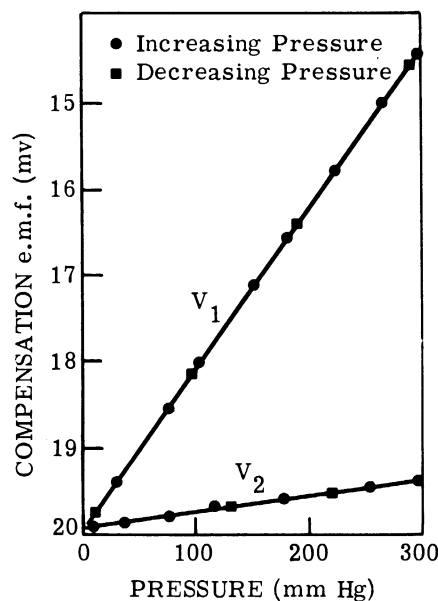


FIGURE 23. MICROBALANCE CALIBRATION CURVES

masses used for this purpose are, for example,  $\text{PrO}_{1.50}$  and  $\text{PrO}_{1.83}$  prepared under standardized conditions (Reference 54). A sample (60 mg) of commercial grade  $\text{Pr}_6\text{O}_{11}$  is suspended from the balance and converted to  $\text{PrO}_{1.50}$  by heating to  $940^\circ\text{C}$  in vacuo for 15 hours. The sample is then cooled to room temperature while being continuously pumped. The compensation voltage of the balance at room temperature under these conditions is recorded as the  $\text{PrO}_{1.50}$  reference mass. Oxygen is admitted to the balance housing up to a pressure of 150 mm, the temperature is slowly increased to  $940^\circ\text{C}$ , and the system is allowed to equilibrate for one hour. The temperature is then reduced to room temperature over a period of about six hours. At room temperature the balance housing is again evacuated to constant mass, and a balance reading is recorded as the  $\text{PrO}_{1.83}$  reference mass. This procedure is used to obtain mass readings under identical conditions of temperature and pressure. The difference between the two readings is considered to be due to the difference in the theoretical mass between these two compositions. Equations 20 and 21 (Section 2.7.4) are used to calculate the sensitivity.

This method must be used with care; the change in the stoichiometry of the decomposition material must be exact and known. For example, if  $\text{KMnO}_4$  is substituted as a calibration solid, one must be sure that oxygen alone is the final decomposition product in the gas phase, and not a mixture of desorbed  $\text{H}_2\text{O}$  and  $\text{O}_2$ .

## 2.7. MEASUREMENT OF AN ISOTHERM

An adsorption isotherm is calculated in three steps, the collection of the raw data, the collection of data to be used to correct for buoyancy effects, and the analysis of the data. These three stages are discussed below for a typical Pr-O isotherm. Other techniques have also been described (Reference 45).

**2.7.1. COLLECTION OF THE DATA.** The process of collecting raw data is similar for every experiment performed on the microbalance. The mass change, which is observed as a change in the voltage across the standard resistor, is monitored as a function of either gas pressure, sample temperature, or time. Some slight modifications in procedure must be made, however, for each kind of experiment. These points will be discussed separately below. The calculations and data obtained for several different types of experiments will be presented.

**2.7.2. GAS PRESSURE-BUOYANCE IRREGULARITIES.** All experiments performed on the microbalance show that at low pressures and high temperatures the apparent mass change of a noninteracting gas and solid with pressure is not linear. This effect, which results from the TMF (thermomolecular flow) of gases along the suspension fibers, occurs most often at pressures of  $10^{-3}$  to 10 torr (Reference 43); at higher pressures the buoyancy (compensation voltage) of a noninteracting mass on the balance is a linear function of the pressure. The deviation caused by TMF may be positive, negative, or a combination of both. The magnitude of the TMF depends on the geometry of the fiber trains and sample bulbs in the heated regions, the temperature gradients they undergo, and the pressure and the conductivity properties of the ambient gas.

The TMF forces may be minimized experimentally. To accomplish this, the furnace is placed so that the sample bulb is at the center of the furnace. The counterbalance side is treated similarly. The magnitude of the TMF force can be adjusted by raising or lowering the furnace on the counterbalance side. The furnace surrounding the sample is never moved. This procedure is followed to maintain an accurate sample temperature. The temperature of the counterpoise furnace may be changed to achieve the same result. Czanderna (Reference 43) showed that the difference between the TMF forces caused by nitrogen and those caused by oxygen is slight. The maximum TMF force is found in the vicinity of 0.01 to 0.3 torr gas pressure. The vacuum point is usually found to be the terminal point of the high pressure extrapolation of the linear portion of the buoyancy curve. The effect is illustrated in Figure 24.

**2.7.3. MEASUREMENT AND CALCULATION OF A Pr-O ISOTHERM.** The first experiment to be discussed is the measurement of the total uptake of an adsorbate, which interacts with an adsorbent, as a function of the gas pressure. An example is the praseodymium oxide-oxygen

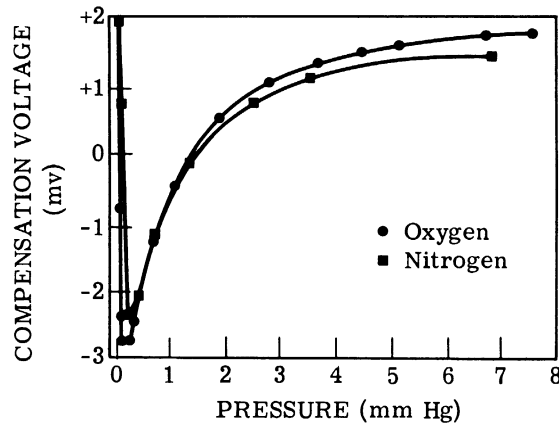


FIGURE 24. THE TMF EFFECT

system (References 46, 54, and 55). The measurement is performed at a relatively high temperature and in an oxygen pressure range of about 150 mm Hg ( $P_{O_2}$  in air is about 150 mm).

The calculation of an isotherm of the Pr-O system requires the measurement of two separate isotherms, one using oxygen and one using nitrogen (Figure 25). Since nitrogen does not react with  $PrO_x$  under the conditions of the experiment, it is used to determine the combined

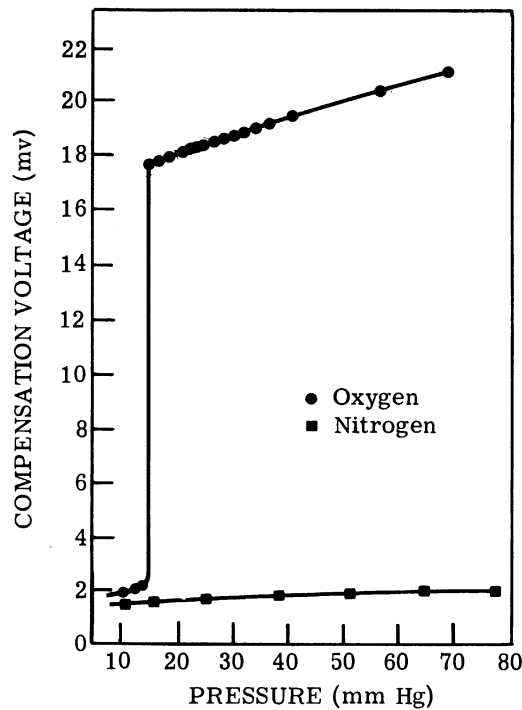


FIGURE 25. RAW DATA OF A TYPICAL Pr-O ISOTHERM

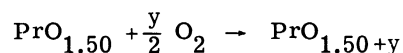
buoyancy and TMF effects on a sample of praseodymia as a function of the gas pressure. To be exact, a noninteracting gas of molecular weight 32, with thermal conductivity properties the same as those of oxygen should be used; however, the difference between the buoyancy effect of nitrogen and that of oxygen is small when each gas interacts physically with an inert mass. The sample of praseodymia is exposed first to nitrogen (noninteraction) and then to oxygen (interaction); the progress of the interaction is measured by calculating the number of moles of oxygen taken up per mole of praseodymia; this is accomplished by graphical subtraction of the two buoyancy functions. Since the system studied in this experiment results only in species in which the ratio of oxygen to praseodymium varies ( $x$  in  $\text{PrO}_x$ ), the difference in buoyancy functions has a simple relation to  $x$ .

A nitrogen isotherm is determined by carefully admitting nitrogen into the evacuated balance housing; the gas pressure is slowly increased to 150 mm at the temperature of the experiment. Approximately 15 minutes is allowed, to establish thermal equilibrium. The pressure is then reduced by removing small quantities of nitrogen (10-mm pressure increments) at ten-minute intervals; the corresponding pressure and compensation voltage are recorded at each stage. Additional points are taken at pressures where TMF is encountered, in order to establish the exact shape of this portion of the isotherm. The system is then evacuated and the sample allowed to establish a constant mass. The above procedure assures that the vacuum points of the nitrogen and the oxygen isotherms will coincide.

After the sample mass is shown to be constant, small increments of oxygen are carefully admitted to the balance system, and each is allowed to equilibrate for periods from a few minutes to several hours. Equilibrium times depend upon the particular experiment and system being studied; the first is usually about an hour.

The compensation voltages of the comparative nitrogen and oxygen isotherms are plotted on a piece of large-scale graph paper. Smooth curves are drawn through the plotted points. To obtain the final adsorption isotherm, the difference between the two curves is obtained at convenient pressure intervals and plotted as a function of pressure.

2.7.4. THE CALCULATION OF  $x$  IN  $\text{PrO}_x$ . The equation for the oxidation of  $\text{Pr}_2\text{O}_3$  is



where  $y$  is the number of moles of oxygen added to the sample per mole of  $\text{PrO}_{1.5}$ . Therefore,  $x = 1.5000 + y$ , where

$$y = K\Delta mv \tag{20}$$

Here  $\Delta mv$  is the difference in millivolts of compensation voltage between the nitrogen and oxygen plots; K is a constant, represented as

$$K = \frac{S}{W} \left( \frac{164.92 \text{ grams PrO}_{1.50} / \text{mole PrO}_{1.50}}{16 \text{ grams oxygen} / \text{gram atom oxygen}} \right) \quad (21)$$

In Equation 21, S is the balance sensitivity in grams per millivolt, and W is the weight in grams of  $\text{PrO}_{1.50}$  used in the experiment. More simply, the total uptake of oxygen may be calculated by multiplying the  $\Delta mv$  by the sensitivity.

The x values are considered reliable to  $\pm 0.0001$  units. The data for a typical determination are illustrated in Figure 26.

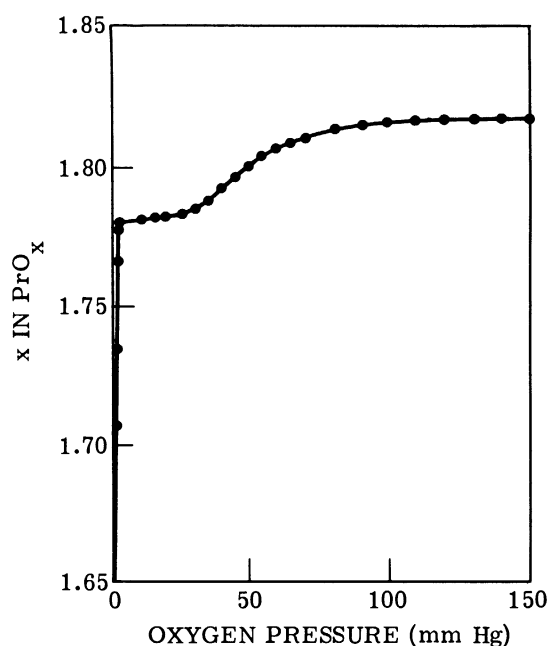


FIGURE 26. A TYPICAL (CALCULATED) Pr-O ISOTHERM

## 2.8. OTHER MEASUREMENTS

2.8.1. KINETIC STUDIES. Besides its use in the study of the total adsorption or reaction of a gas with a solid as a function of gas pressure, the microbalance described above has several other interesting applications. One such application is the measurement of kinetic processes. The oxidation of  $\text{PrO}_{1.50}$  will be discussed as an example (see also Reference 56).

In the case discussed below, the rate of uptake is determined at essentially constant pressure. The volume of the working system is about two liters, and the sample size is about 50 mg.

The amount of gas reacting, at say 10 mm or above, is so small that a pressure difference between the initial and final pressure conditions cannot be determined with a mercury manometer. Also, if a manometer similar to the one described in the volumetric adsorption section (Section 1.3.3) is used, essentially constant volume is also maintained.

Recall that when the total uptake is determined as a function of pressure, two curves are needed to obtain the amount of gaseous oxygen which has reacted. Since the kinetic data are taken under isothermal and isobaric conditions, they describe the rate at which the chemical system moves along a vertical line between the curves for nitrogen and oxygen.

A buoyancy correction at constant temperature and pressure enters into the calculations as a constant to be subtracted from all of the recorded mass increases. This "constant" varies as the pressure at which the kinetics is studied, and is a result of the slope of the nitrogen buoyancy curve.

To obtain kinetic data, a nitrogen isotherm is determined, as described before, around the value of the oxygen pressure to be considered. Then the nitrogen is carefully pumped off and oxygen is admitted (in increments if necessary) until the operating pressure is reached. The moment of the first addition is taken as zero time. In this case about three to five minutes is needed for the gas to damp the balance and free it from oscillations before meaningful data can be recorded. The compensation voltage and time are recorded as the indicator hook passes the null position. When the operator has become familiar with the system, the potentiometer can be set to compensate for a prearranged voltage and the time recorded with increased accuracy. The process is continued as long as it is considered desirable.

Equations 20 and 21 are used to transform the raw data to convenient units. As before,  $\Delta mv$  is obtained by subtracting the nitrogen function from the oxygen function. Data taken in such a measurement are given in Figure 27 as a plot of millimoles of oxygen per mole of  $\text{PrO}_{1.50}$  versus the logarithm of time.

**2.8.2. DETERMINING SURFACE AREA FROM NITROGEN ADSORPTION.** The microbalance may be used to measure the surface areas of powders. As mentioned in Section 1.2, if the amount of a gas adsorbed in a monolayer on the surface of a solid can be calculated, and the area occupied by a single gas molecule is known, the surface area can be calculated. After the variation of surface coverage as a function of pressure has been established, the data may be interpreted in various ways in order to calculate the amount of gas in a monolayer. The Point B method (Reference 25) will be illustrated in this discussion, although the data could be treated in terms of the B.E.T. multilayer theory as well. Data from a measurement of a sample of  $\text{TiO}_2$  will be used as an illustration.



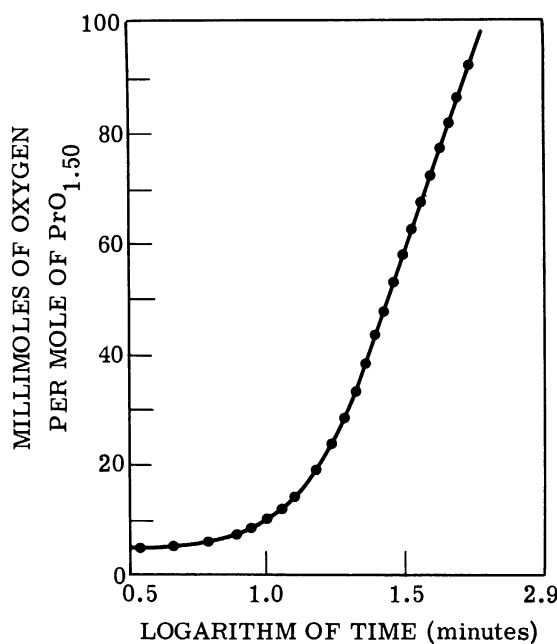


FIGURE 27. RATE OF OXIDATION OF  
 $\text{Pr}_2\text{O}_3$

To measure surface area, about 100 to 200 mg of sample is suspended from the balance in the manner described previously. The balance housing is then evacuated, and the sample temperature is raised to  $500^\circ\text{C}$  (see Section 1.5.2). The heating is continued until no further mass loss is observed. The furnace is removed, and a nitrogen bath is placed around the fused silica envelope that surrounds the sample. A few millimeters of helium pressure is then established inside the housing, and the system is allowed to equilibrate at  $78^\circ\text{K}$ ; the system will reach thermal equilibrium in a few minutes. The helium is then removed and the system is pumped at  $78^\circ\text{K}$  until no further mass changes are observed. Dry nitrogen is then admitted in increments to the balance housing, and the change in compensation voltage, a function of the total equilibrium pressure, is recorded. The first increments of gas must be added very slowly, or the balance may strike the arrest, shift its position, and thus change the reference point of the experiment.

If a plot of the amount of nitrogen adsorbed versus the nitrogen gas pressure is made, the linear portion of the isotherm can be extrapolated to the ordinate. The point at which the experimental curve breaks away from the linear portion of the isotherm is taken as Point B.

The specific surface area in square meters/gram is calculated from the equation

$$\text{specific surface} = K(X/Y) \quad (22)$$

where X is the number of micrograms of N<sub>2</sub> adsorbed at Point B, and Y is the sample weight in milligrams. K is a constant for nitrogen and is equal to 3.48; it is represented as

$$K = \frac{\sigma_{N_2} N}{M} \tag{23}$$

where N is Avogadro's Number,  $\sigma_{N_2}$  is the cross sectional area of an adsorbed N<sub>2</sub> molecule, and M is the gram molecular weight of N<sub>2</sub>. A typical set of data is given in Table XI and illustrated in Figure 28.

TABLE XI. SURFACE AREA DATA FOR THE ADSORPTION OF NITROGEN ON RUTILE AT 78°K

Nitrogen Pressure (mm Hg)	Nitrogen Adsorbed (μg)	Nitrogen Pressure (mm Hg)	Nitrogen Adsorbed (μg)
10 <sup>-6</sup>	0	123.1	1375
0.0025	123	150.8	1454
0.28	626	180.3	1532
0.67	706	223.0	1642
1.97	821	267.9	1752
3.3	890	383.7	2074
8.7	978	486.0	2585
16.0	1036	100.5	1319
23.2	1070	23.5	1072
47.0	1178	7.7	926
77.8	1255	10 <sup>-6</sup>	14
107.1	1335		

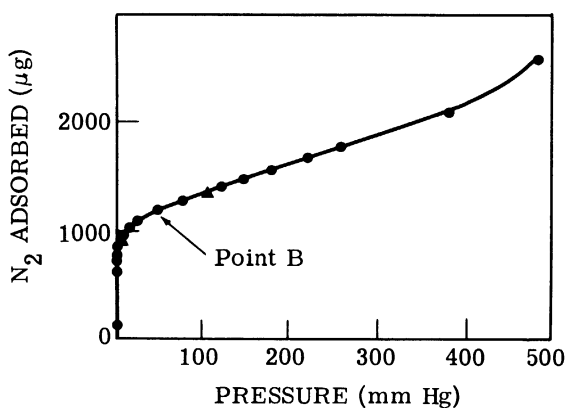


FIGURE 28. ADSORPTION OF NITROGEN ON RUTILE AT 78°A

It must be noted that in order to calculate the masses of nitrogen adsorbed at various pressures, it is assumed that under the experimental conditions no correction is needed for the buoyancy effect of a noninteracting gas on the sample. The matter in question is not the TMF calibration, mentioned earlier, but the slope of the linear portion of the compensation voltage-pressure curve of a noninteracting gas. If this slope is very small, as it is in the case illustrated below, the amount of nitrogen adsorbed as a function of the pressure may be calculated as

$$\mu\text{g of N}_2 = (\Delta\text{mv}) (\text{sensitivity, } \mu\text{g/mv}) \quad (24)$$

where  $\Delta\text{mv}$  is the difference between the value of the compensation voltage at the reference point of no adsorption ( $78^\circ\text{K}$ ,  $10^{-6}$  mm Hg) and the value of the compensation voltage at succeeding equilibrium values of the total pressure.

If a correction is needed, the variation of the compensation voltage with nitrogen pressure at  $78^\circ\text{K}$  is recorded (1) when the empty sample bulb alone is on the balance, and (2) when a sample is present. The reference points of the curves of the two experiments are then superimposed on the same piece of graph paper and the curves graphically subtracted.  $\Delta\text{mv}$  in Equation 24 is now the difference between these two curves.

**2.8.3. MAGNETIC SUSCEPTIBILITY.** The microbalance may also be used to measure magnetic properties (Reference 57) of various substances by what is known as the Gouy method (Reference 58). A sample is placed between the poles of an energized magnet and the effect on it is observed. If a sample in a thin-walled tube is suspended between the poles of a magnet so that the lower end of the tube is cut by the maximum flux, the substance will be repulsed by or drawn into the field of the magnet. Paramagnetic substances experience a downward force, and diamagnetic substances experience an upward one. The force can be conveniently measured as a change in weight ( $\Delta W$ ) if the sample is suspended from a balance.

For samples that weigh one gram or less, the values of  $\Delta W$  range from a few micrograms to several hundred milligrams. These limits place the measurement of susceptibilities in the region of sensitivity and capacity of the microbalance. The susceptibility can be calculated as follows:

$$d_1\chi_1 - d_2\chi_2 = \frac{2g\Delta W}{H^2 A} \quad (25)$$

where  $d_1$ ,  $\chi_1$  and  $d_2$ ,  $\chi_2$  are the densities and mass susceptibilities of the sample and of the surrounding atmosphere, respectively;  $g$  is the acceleration due to gravity;  $H$  is the magnetic field intensity; and  $A$  is the cross-sectional area of the sample. To obtain  $\Delta W$ , Equation 24 is used. (Variations of the Gouy method are discussed by Dodd and Robinson, Reference 57.)

Several standard samples of known magnetic susceptibility have been used to calibrate the field of a magnet. Powdered, crystalline ferrous ammonium sulfate or a solution of nickel chloride is commonly used, and  $\text{HgCo}(\text{CNS})_4$  (Reference 59) has also been used. If the field strength is known and a substance of known susceptibility is measured, the balance sensitivity may be calculated by using Equations 24 and 25. However, this method is not as reliable as the absolute method (Section 2.6.1). The use of the microbalance to measure magnetic susceptibilities has been discussed by Kern (Reference 60) and Turner (Reference 61).

An additional note must be made about this measurement and the microbalance. It is possible for the field of the magnet to interact with the Alnico needle and give spurious results; the effect of the interaction can be reduced by calibration and/or shielding, or by using small fields.

## 2.9. SUMMARY

The microbalance has several important advantages.

- (1) Compared with other precision instruments, it is inexpensive and easy to maintain.
- (2) Although the balance must be handled with care, the construction is very rugged.
- (3) Small errors in the alignment of the balance appear to have no significant effect on the operation of the balance.
- (4) The long-term stability of the balance calibration is excellent.
- (5) A precision of  $10^{-8}$  gram is readily attained.

The microbalance may be used for many different experiments. However, some of its properties have not been explained or understood (Reference 62), and for this reason applying it to new problems may present new difficulties. More research needs to be done on this balance and balances in general so that their applicability may be extended. In the meantime, the device described above will serve to measure differences in mass in the microgram region.

## Appendix

### CROSS-SECTIONAL AREAS OF ADSORBED MOLECULES

Table XII lists values for the cross-sectional areas of various molecular types used in adsorption research. It must be noted, however, that the data on one species but from different sources do not always agree. Irregularities in the surface of the adsorbent are a determining factor in the effective cross-sectional area occupied by the adsorbate molecule. The values of 16.2 and 19.5  $\text{\AA}^2$ /molecule, for nitrogen and krypton respectively, are commonly used. It is recommended that the original papers be consulted before the values below are used for determinations where the accuracy is critical.

TABLE XII. CROSS-SECTIONAL AREAS OF ADSORBED MOLECULES

Particle	Temperature (°C)	Area (Å <sup>2</sup> /molecule)	Adsorbent	Reference
Ne	-253	10.0	Ni foil	63, 64
Ar	-195	13.7	(calculated)	65
	-195	15.4	glass spheres	65
Kr	-195	19.5	oxides and porous glass	30
Kr	-195	15.2	(calculated)	29
	-195	20.8	glass spheres, metals, and oxides	29
O <sub>2</sub>	-183	14.6	porous glass and silica gel	64
	-183	14.1	(calculated)	3
H <sub>2</sub>	-253	8.3	Ni foil	63, 64
H <sub>2</sub> O	25	10.6	oxides	66
	24	10.6	oxides	27
	26.5	10.8	(calculated)	65
D <sub>2</sub>	-253	7.2	Ni foil	63, 64
F <sup>-</sup>		12.9		67
Cl <sub>2</sub>	32-33	21.1	metals	68
Cl <sup>-</sup>		22		67
I <sub>2</sub>		22.1	BaCl <sub>2</sub> , CaF <sub>2</sub>	67
N <sub>2</sub>	-195.8	16.2	(calculated)	3
N <sub>2</sub> O	-78	20.4	2 charcoals and a carbon black	64
	-80	16.8	(calculated)	3
NO	-150	12.5	(calculated)	3
NO <sub>2</sub>	32-34	15.0	metals	68
NH <sub>3</sub>	-32.5	15.4	porous glass	65
	-32.5	13.8	(calculated)	65
CO	-183	16.8	(calculated)	3
CO <sub>2</sub>	-78	14.2	(calculated)	65
	-78	20.1	porous glass	65
CO <sub>2</sub>	-56.6	17.0	(calculated)	3
CH <sub>4</sub>	-183	16.0	Ni foil	63, 64
		17.2	(calculated)	69
C <sub>2</sub> H <sub>2</sub>	-78	22.2	porous glass	65
	-78	15.2	(calculated)	65

Particle	Temperature (°C)	Area (Å <sup>2</sup> /molecule)	Adsorbent	Reference
C <sub>2</sub> H <sub>6</sub>	-183	23	KCl and NaCl	70
	-183	20.5	chrome-plated Ni strips	71
	-183	24	TiO <sub>2</sub>	70
		22.1	(calculated)	69
C <sub>3</sub> H <sub>8</sub>		27.4	(calculated)	69
C <sub>4</sub> H <sub>8</sub>	0	42.7	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	29
	0	30.5	(calculated)	29
n-C <sub>4</sub> H <sub>10</sub>	-78	43.4	glass spheres and metals	29
	-78	29.7	(calculated)	29
	0	46.9	tungsten powder and ZnO	29
	0	32.1	(calculated)	29
	0	52, 41, 42	carbon and Zn dusts	72
	0	49	porous glass	65
	0	56.6	glass spheres	73
C <sub>6</sub> H <sub>6</sub>	25	27.0	titanium oxides	66
n-C <sub>7</sub> H <sub>16</sub>	24	55	oxides	27
	24	44	graphite	27
CH <sub>3</sub> OH	25	12	lignite	74
C <sub>2</sub> H <sub>5</sub> OH	0	20	glass spheres	19
C <sub>3</sub> H <sub>7</sub> OH	25	20	oxides	66
	25	27	(calculated)	66
	25	20	oxides	27
(CH <sub>3</sub> ) <sub>2</sub> CO	25	26.9	(calculated)	7
CHCl <sub>2</sub> F	-78	24.7	(calculated)	29
	-78	37.5	glass spheres, metals, and oxides	29
	0	26.4	(calculated)	29
	0	40.1	glass spheres, met- als, and oxides	29
C <sub>2</sub> H <sub>5</sub> Cl	0	23.9	(calculated)	75
	0	26.1	graphite	75
CS <sub>2</sub>	0	23	(calculated)	72

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