Surface-Area Determination by Adsorption of Nitrogen from Nitrogen-Helium Mixtures [1]

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A new apparatus and technique, in which vacuum pumps and associated equipment are not required, have been developed for the determination of the adsorption of nitrogen from mixtures with helium for use in the determination of surface area. The sample is heated initially in a stream of helium. The adsorption of helium is negligible at the temperatures concerned. The gas mixture is cycled repeatedly over the adsorbent until no further change in pressure is observed. Temperature equilibration is attained rapidly. It is shown that thermomolecular pressure differences are negligible under the conditions of the experiment. Surface-area determinations by the simplified technique are in good agreement with results obtained by the conventional volumetric method when the same adsorbents are used with various residual helium pressures.

I. Introduction

The volumetric method for the determination of gas adsorption is still the most popular method in use today. Since the investigations of Titoff [1] [3] and of Homfray [2] in 1910, the apparatus and the technique employed for gas adsorption have remained essentially unchanged. Certain refinements have been introduced, such as the substitution of mercury traps for stopcocks by Coolidge in 1924 [3] and also by Goldmann and Polanyi in 1928 [4], but such refinements did not change the basic technique and procedure and tended to make the apparatus more complicated.

Current interest in the measurement of the adsorption of nitrogen at low temperatures is in the use of the data to determine surface areas. The latter are based upon determinations of the volumes of nitrogen that are necessary to cover the surfaces with a monolayer of the gas. Relationships to do this have been developed by Brunauer, Emmett, and Teller [5]. With certain assumptions as to the packing of the nitrogen molecules, the extent of the adsorbing surface may then be estimated.

The conventional gas-adsorption apparatus in use today consists of (1) an adsorption cell to hold the adsorbent sample, (2) a gas buret (usually of the multibulb variety), (3) a manometer, and (4) a pumping system that includes a mechanical pump, diffusion pump, liquid-air trap, and McLeod gage. The system is first evacuated to remove air, water, and other interfering impurities from the adsorbent. The latter is maintained at a temperature sufficiently high to assist in the expulsion of desorbable impurities, yet not so high as to bring about an irreversible change in its structure. Following the degassing treatment, the sample is cooled to the temperature at which the adsorption is to take place, and a determination of the "dead space" is made with purified helium. This space consists of the

volume within the adsorption tube not occupied by the sample, that is, the space between the particles, and the volume of the connective tubing that joins the adsorption cell with the buret manifold. It is customary to admit purified helium to the buret system and to measure its volume and pressure before and after exposure to the adsorption cell containing the sample. The dead space is computed from these data by application of the gas laws.

It is necessary next to exhaust the helium from the system before the adsorbate (usually nitrogen) can be admitted. Customarily, the sample is allowed to warm up during the evacuation to assist in the removal of helium. The procedure for introducing the gas is similar to that outlined for the introduction of helium. When a nitrogen-adsorption isotherm is to be used for determining surface area according to the "free-surface" equation of Brunauer, Emmett, and Teller [5], it is important to confine all equilibrium pressures to the region where the equation is applicable. This is usually valid below relative pressures of about 0.3, where the relative pressure is the ratio of the pressure to the saturation pressure at the temperature of the experiment. A minimum of two points is required to determine the straight line resulting from a plot of $p/[V(p_0-p)]$ against p/p_0 (relative pressure), where p is the equilibrium pressure, p_0 the saturation pressure, and V the volume of nitrogen adsorbed. However, it is good practice to obtain four points for check purposes. The reciprocal of the sum of slope and intercept of this straight line is directly proportional to the surface area. In many cases the multibulb buret can be used to obtain successive points on the adsorption isotherm with only a single initial filling of the buret.

The simplified technique described in this paper [6] is based upon the selective adsorption of nitrogen from nitrogen-helium mixtures. Because of this phenomenon, the following advantages are possible: (1) the entire evacuation system can be eliminated, (2) equilibria are attained rapidly by repeatedly cycling the gas mixture through the sample, (3) time is saved by not having to wait to remove the helium or to recool the adsorption tube before admitting nitrogen.

The description of the new apparatus and the account of the new procedure will be given in some detail. The instructions are intended to be sufficient for use by others not too expert in this field of physical chemical measurements.

II. Design of Apparatus

A diagram of the apparatus is shown in figure 1. The adsorption tube, T, consists of a glass tube 30 cm in length and 12 mm in diameter fitted at the top with a ground-glass joint. The inner member of the joint extends downward to within 3 or 4 cm of the bottom of the tube, where it is rounded off like a test tube. The annular space between the outer tube and the extension of the inner member constitutes part of the dead space, which should be kept as small as possible [7]. For this reason the fit should be extremely snug. The sample is contained in the bottom of the adsorption tube. If the sample is finely ground, a small pad of glass cotton placed both above and below the sample will hold it intact. The gas is brought in contact with both top and bottom of the sample by capillary tubing, which terminates in ball and socket joints. One lead connects with the annular space just below the ground-glass joint of the adsorption tube, and the other lead extends from the bottom of the tube where it forms a U-bend, as shown in figure 1. The tube is purposely made long in order that the extremes in temperature to which the sample is exposed do not affect the lubricant of the joints and stopcocks at the top.

The other half of each ball and socket joint is sealed to capillary tubing that communicates to the tops of two equal-volume cylindrical burets, P and S. These are made of 30-mm tubing and are calibrated to contain a volume of about 200 ml. The volume of P is bounded at the top by stopcocks I and E and at the bottom by the graduation mark A. The volume of S includes the space between graduation marks B and C. Leveling bulbs, L and M, are joined to the bottoms of S and P, respectively, by means of rubber tubing. Air traps, not shown in figure 1, are located at the lower extremities of S and P for the purpose of catching any stray bubbles of air that might be introduced through the rubber connections from the leveling bulbs or from gases entrapped in the mercury. A stopcock, D, located below graduation B serves as a positive cut-off for holding the mercury level either at mark B or C while a pressure measurement is being made. All pressure measurements are made relative to atmospheric. A sidearm made of 10-mm tubing is connected to bulb M and is used as one arm of the manometer with a vernier-adjusted slide on the millimeter scale, R. The other mercury level is in the buret system, and readings are only made when the mercury level is at marks A and B or C. Atmospheric pressure is determined at frequent intervals. The purified gases, helium or nitrogen, are introduced through stopcock E. Stopcock I, located between the primary buret P and the adsorption tube, enables pressure measurements to be made of the gases in the primary buret before exposure to the sample Stopcock X serves as an exit to the atmosphere.

III. Experimental Procedure

The sample is first freed from interfering impurities, such as air and moisture, by heating it in a continuous stream of helium. The helium in tanks (obtained from Bureau of Mines, Amarillo, Tex.) was of a high grade of purity and might be used as received. As an added precaution, it was further treated by passage through a trap containing activated charcoal surrounded by liquid air. The burets are kept completely filled with mercury so that all of the evolved gases are carried along with the helium through stopcock X (fig. 1), where they escape into the atmosphere. An electric sleeve furnace fits around the lower portion of the adsorption tube, and aluminum foil is placed in position to serve as a heat shield for the greased joints above, as well as for the burets at either side.

After degassing, stopcock X is closed and helium is permitted to enter P by lowering M slowly until the primary buret is filled. Stopcock E is then closed, thus isolating a quantity of helium within the system. The sleeve furnace is removed and replaced with a Dewar flask containing liquid oxygen.[4] Liquid oxygen was prepared according to the method described by Lane and Watson [13]. Care was taken to maintain the level of liquid oxygen by frequent additions. The mercury level in S is adjusted to mark C and stopcock D closed. The mercury level in P is brought to mark A, and the level in the side arm of M is read against the vernier slide on R. This scale reading, when added to the atmospheric pressure and diminished by the null-point value of the scale, gives the pressure of helium in the system. The level of mercury is next dropped from C to B by opening stopcock D and lowering bulb L, thus allowing helium to fill the secondary buret. Stopcock D is again closed before attempting to bring back the mercury level of the primary buret to mark A. When this is done, the pressure is again measured. These data suffice to determine the dead space. However, it is recommended that the process be repeated for check purposes after first expelling a portion of the helium from the system. The dead-space volume may be calculated according to the equation:

$$V/T = [p_2/(p_1-p_2)](V_2/T_0) - V_1/T_0, \qquad (1)$$

where V = geometric volume of dead space
V_1 = geometric volume of buret P
V_2 = geometric volume of buret S
T = temperature of refrigerant bath (deg K)
T_0 = room temperature (deg K)
p_1 = pressure of system when helium is confined to primary buret and adsorption tube
p_2 = pressure of system when helium is expanded to include secondary buret.

[4] Liquid nitrogen may equally be used if it is desired to perform the measurements at the lower temperature.

The pressure of helium may be further reduced, if desired, before continuing with the determination of the nitrogen adsorption by raising the leveling bulb M until the helium in the system is compressed above atmospheric, then opening momentarily the exit stopcock. The residual pressure of helium is finally measured with the mercury levels at marks A and C.

Equation 1 assumes that all the volume between C and I is at the temperature T. However, the volume not at T (i. e. not immersed in the bath) is deliberately made as small as practical. Moveover, the small error resulting from this assumption is almost compensated by the use of the identical procedure when nitrogen is introduced.

During all the preceding steps, stopcock I is left in the open position. It is closed immediately after the residual helium pressure is measured. The leveling bulb M is raised so as to bring the helium in buret P nearly to atmospheric pressure. With some experience this enables a better control of the volume of nitrogen to be admitted. Nitrogen gas for the adsorption measurements was purified by passing tank nitrogen first over heated copper (450° C) supported vertically in a column, and second by passage through tubes containing Ascarite and Anhydrone. The purified nitrogen at atmospheric pressure is admitted to the primary buret through stopcock E, care being taken that the mercury level in P remains above that in M so that the pressure in P is below atmospheric, and no helium is lost in the process. Sufficient nitrogen is introduced to yield a measurable increase in pressure over that of the residual helium after equilibrium is established with the adsorbent. Stopcock E is then closed, the mercury level brought to mark A, and the pressure measured as before. The difference between this total pressure and the residual or partial pressure of the helium previously measured gives the pressure of nitrogen introduced into the buret system. Stopcocks I and D are now opened. By raising bulb M and lowering L, the gas mixture is caused to pass from buret P through the adsorbent T and into buret S such that the latter is filled with gas at approximately the same rate that P is emptied. When P is completely emptied of gas and S filled, the positions of the mercury levelling bulbs are reversed, which causes the gas mixture to pass from S through the sample and back into P. This constitutes one complete cycle of exposure. After several such cycles (four or five) it is usually found that the pressure (measured with mercury levels at marks A and C) no longer decreases. This is recorded as the equilibrium total pressure. The equilibrium pressure of nitrogen is obtained by subtracting from this value the residual pressure of helium (corrected, if necessary, for changes in room temperature). The isolating stopcock I is then closed; a second increment of nitrogen is drawn into the primary buret and the resultant pressure measured as before. The cycling exposure to the sample is repeated according to the technique already described, and the second equilibrium total pressure is obtained. Although two points on the isotherm

are all that are necessary to determine the straight line used to compute the surface area, it is recommended that three or preferably four points be obtained to make evident an unusual error of measurement.

The determination of the liquid oxygen or nitrogen temperatures and the necessary vapor pressure of oxygen or nitrogen were computed from published results.[5] The vapor pressure of nitrogen in millimeters as a function of the absolute temperature (T) in the neighborhood of its boiling point is given by eq 2 [8]

$$\log p_{N_2} = -334.64/T + 7.5777 - 4.76T \times 10^{-3}. \quad (2)$$

The vapor pressure of oxygen is given by eq 3, which is valid over the same range of temperature [9]

$$\log p_{0_2} = -419.31/T + 8.1173 - 6.48T \times 10^{-3}. \quad (3)$$

Utilizing eq 2 and 3 for adsorption at liquid oxygen temperatures, it was convenient to plot p_{N_2} as a function of p_{0_2}, with the corresponding temperatures marked along the resultant curve itself. The vapor pressure of the oxygen was taken as barometric pressure; hence, it was necessary only to locate atmospheric pressure along the abscissa (p_{0_2} axis) to obtain the temperature of the bath and the corresponding vapor pressure of nitrogen. As saturation pressure is of the order of magnitude of 2,700 mm, equilibrium partial pressures of nitrogen up to atmospheric during an adsorption determination all fall within the range where the free-surface equation of Brunauer, Emmett, and Teller [5] is valid (relative pressure is less than 0.3).

The pressure readings made from day to day were corrected for ambient temperature differences by taking into account the difference in thermal expansion between mercury and the graduated scales.

Correction must be made for the nonideal behavior of nitrogen above the sample in the adsorption tube. An approximation of sufficient accuracy for adsorption measurements of this type is obtained by multiplying the observed volume of dead space V by the correction factor $[1 + \alpha p]$, where p is the pressure in millimeters, and α is a constant for a given gas at a particular temperature [10].

This same factor may also be derived from the evaluation of the second virial coefficient or from viscosity data [11]. This treatment has been summarized in an unpublished report by William S. Benedict [12]. These results are compared in table 1 with results quoted by Emmett and Brunauer [10]. The correction must be made, since its magnitude may be as large as 5 percent, but the relative discrepancy among the correction factors from the various sources is small even at atmospheric pressure. For example, the disagreement between the two extreme values for nitrogen at 77.3° K and 760-mm pressure amounts to only 1.5 percent.

[5] More recent data on the vapor pressures of oxygen and nitrogen have been given in tabular form compiled from a critical study of all data up to 1949 [17, 18].

TABLE 1. *Volume correction factor α for nonideal gases*

	Emmett and Brunauer [10]	2d Virial coefficient [11]	Viscosity data [11]
	mm^{-1}	mm^{-1}	mm^{-1}
Nitrogen:			
at 77.3 °K	6.6×10^{-5}	5.0×10^{-5}	4.5×10^{-5}
at 90.1 °K	3.8	3.3	2.9
Oxygen:			
at 77.3 °K		6.3	5.3
at 90.1 °K	4.2	4.2	3.4
Methane:			
at 90.1 °K		7.1	6.6

IV. Results and Discussion

The basic assumptions of the proposed method are that nitrogen is quantitatively adsorbed from nitrogen-helium mixtures, and the helium remains in the gas phase. The most direct test for the validity of these assumptions is to compare the results of surface areas determined by means of the simplified technique with results for the same samples by the conventional method (where no helium is used during the nitrogen adsorption). Samples of materials varying widely both in composition and surface area were selected for these tests. Furthermore, the residual pressure of helium in the nitrogen-helium mixture was varied in repeated runs with the same sample and in one case (Bone Char 32) exceeded half an atmosphere. Although such practice is not recommended in routine measurements, it was done here merely to emphasize the complete lack of dependence of nitrogen adsorption upon the presence of helium. The results are shown in table 2. Liquid oxygen was used as refrigerant except where indicated. The comparison of the values for surface area given in the last two columns of table 2 shows the good agreement between the two methods.

TABLE 2. *Comparison of surface areas determined by the simplified method with the conventional method*

Material tested	Simplified technique		Surface area (conventional method)
	Residual helium pressure	Surface area	
	mm Hg	m^2/g	m^2/g
Char 32 (16 × 18 mesh)	79	61	62
	80	60	59
	293	62	----
	405	61	----
Silica gel	92	700	714
	211	705	----
Coconut shell charcoal	271	1297	1292
[a] TiO$_2$	197	7.4	7.5
[a] Monterey shale	211	89	[b] 87
Activated clay	208	121	126
Diatomaceous earth	203	53	55
Darco G-60	206	1295	1305

[a] Samples furnished and independently measured by R. L. Blaine.
[b] Liquid nitrogen used as refrigerant.

The possibility of introducing an appreciable error due to thermomolecular diffusion effects was considered during the development of the simplified technique. As the manometer is connected to the buret system, which is at room temperature, it is assumed that the same pressure exists above the sample in the refrigerated adsorption tube. This assumption is not strictly valid, and the error may conceivably reach appreciable proportions as the total pressure is diminished. This phenomenon has been investigated for individual gases by Weber (et al.) [14 to 16] from theoretical considerations. The general equation derived in Weber's investigation was simplified and a relationship deduced for estimating the lowest pressure that would still be compatible with a pressure difference amounting to no more than a predetermined percentage of the pressure. This relationship is given as follows

$$\frac{\Delta p}{p} = \frac{6k_1(_1\lambda_0)^2}{(1+n)\pi R^2 p^2}\left[\left(\frac{T_1}{T_0}\right)^{2+2n} - \left(\frac{T_2}{T_0}\right)^{2+2n}\right], \quad (4)$$

where

Δp = thermomolecular pressure difference
p = manometer pressure in microbars
R = radius of the connective tubing in centimeters
T_1 = temperature of the warm end of the connecting tube (room temperature, °K)
T_2 = temperature of the cold end of the connecting tube (adsorbent temperature, °K)
T_0 = 273.1 °K
$k_1, n, _1\lambda_0$ = parameters depending upon the gas employed.

The values of k_1, n, and $_1\lambda_0$ for nitrogen are given by Weber as 1.40, 0.41, and 5.91 and for helium 1.32, 0.147, and 17.85, respectively. By setting $\Delta p/p = 0.01$ in eq 4 and using $T_1 = 300°$, $T_2 = 90°$, and $R = 0.05$, it is possible to solve for p (converting pressure to mm Hg). For these conditions p_{N_2} is found to be 1.37 mm Hg and p_{He} 4.27 mm Hg.

It is seen that an error no greater than 1 percent of the total pressure would result by virtue of the thermomolecular pressure difference (thermal diffusion) as long as the total pressure of nitrogen by itself or helium by itself remained greater than the values shown above. Although no theory has yet been advanced to predict the thermomolecular pressure difference in mixtures of gases, it is reasonable to expect that for nitrogen-helium mixtures the error should be of the same order of magnitude as for the separate gases. Furthermore, as the free surface equation of Brunauer, Emmett, and Teller is usually valid within the relative pressure region between 0.1 and 0.3, and since p_0 for nitrogen at liquid oxygen temperatures is of the order of magnitude of 2730 mm, the partial pressures of nitrogen need not be less than 270 mm. At this pressure the error due to thermomolecular pressure difference must certainly be negligible. Even at liquid nitrogen temperatures, it can be shown from eq 4 that the pressure limit for 1-percent error is virtually the same as at liquid oxygen temperatures. A partial pressure of nitrogen of 76 mm corresponds to a relative pressure of 0.1. Here, too, the correction is negligible.

The final step in completing each cycle of exposure prior to reading the pressure consists in passing the
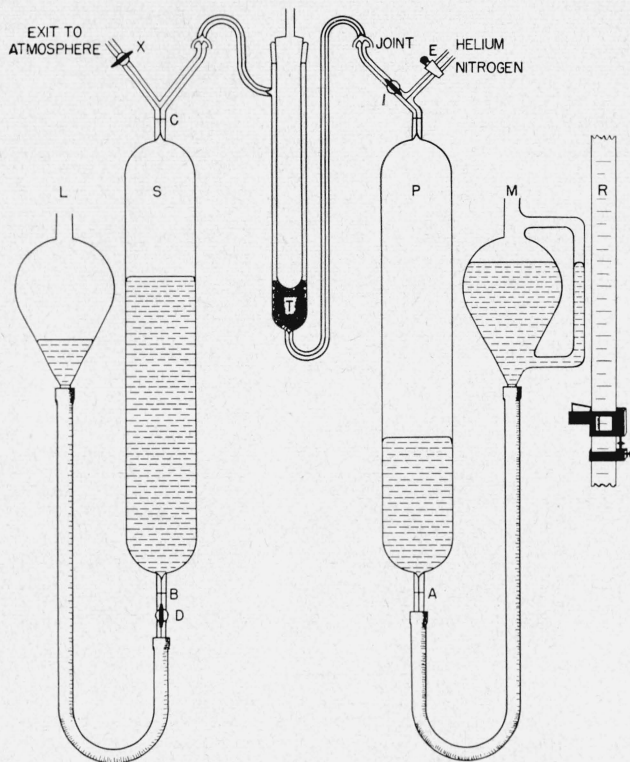
FIGURE 1. *Simplified apparatus for adsorption of nitrogen from helium mixtures.*

gas mixture from S through T into P (see fig. 1). Sufficient heat must be conducted away from the gas mixture on its way to the sample to prevent a rise in temperature of the latter during the half-cycle preceding each pressure measurement. The heat requirements may be estimated from the volume of gas mixture to be cooled, its heat capacity, and the temperature change. If the buret system were completely filled with gas at atmospheric pressure, 200 ml would correspond to about 9 millimoles. Its heat capacity would be of the order of 6 cal/mole (7 cal/mole, if all nitrogen; 5 cal/mole, if all helium). Hence, a temperature change of 210° in cooling from 300° to 90° K would require a heat transfer of only about 50 cal. As the latent heat of vaporization of liquid oxygen at its boiling point is 51 cal, about 1 g of oxygen is boiled away in each half-cycle of exposure. The level of liquid oxygen was maintained by frequent additions.

Furthermore, the gas mixture must pass a distance of 10 cm below the surface of the liquid oxygen through the annular space before it reaches the sample. The annular ring is 1 cm in diameter, and the wall thickness of the glass is 1 mm. If the time required to complete one half-cycle is 3 mins, it can be shown from heat tranfer considerations that the gas, as it reaches the sample, is virtually at the same temperature as the bath.

The feasibility of using nitrogen-helium mixtures has been amply demonstrated here, but by the same token, other adsorbates mixed with helium might also be used. It is believed that the greatest single achievement of the simplified technique is the complete elimination of the vacuum pumps and the associated equipment. It is now both feasible and practicable to house the entire assembly in a compact unit and thus make possible a portable apparatus.

V. Summary

1. A simple apparatus requiring no vacuum system has been developed for the determination of surface area by the volumetric adsorption of nitrogen at low temperatures.

2. The presence of helium, even at a relatively high partial pressure, does not affect the adsorption of nitrogen insofar as surface area determinations are concerned.

3. Comparison of the results obtained for surface area by the simplified technique with those obtained by the conventional method shows excellent agreement over a wide range of adsorbents.

4. The effect of thermomolecular pressure difference was investigated and found not to be appreciable under the experimental conditions of the measurements.

VI. References

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