

Adsorption of Nitrogen on Carbon Adsorbents at Low Pressures between 69° and 90° K

Juan de Dios Lopez-Gonzalez,¹ Frank G. Carpenter,¹ and Victor R. Deitz

Nitrogen adsorption isotherms were determined on three carbon adsorbents (two bone chars and an activated coconut shell charcoal) at three temperatures between 69° and 90° K and at relative pressures from 10^{-7} to 0.9. A cryostat was used to obtain temperatures below the normal boiling point of liquid nitrogen. The attainment of steady pressure readings at very low pressures required considerably more time than at higher pressures. Corrections for thermomolecular diffusion were found to be appreciable at pressures below one millimeter of mercury.

At relative pressures below 10^{-4} , the amount of nitrogen adsorbed depended upon the condition of the surface in regard to previous adsorption of nitrogen. A technique involving a series of consecutive adsorptions at low temperatures and outgasings at room temperature led to a reproducible isotherm at low pressures. These data could be represented by a Freundlich equation. The Brunauer, Emmett, Teller surface areas of the carbon adsorbents were also determined.

1. Introduction

During the last decade the main emphasis of research in gas adsorption has been on the evaluation of surface area. The success attained has been due largely to the development of the Brunauer, Emmett, Teller (B.E.T.) theory of multimolecular adsorption and to the constructive critical work that followed. The fact that the B.E.T. equation was inapplicable to data at relative pressures² below 0.05 was of little consequence because adsorption measurements in this region were not needed in the surface-area determinations. Experimental difficulties have been an additional cause for the scarcity of data on physical adsorption at low relative pressures.

Adsorption data at very low pressures are necessary for the calculation of thermodynamic functions of the adsorbed phase. These functions are of special interest in the range of very low surface-coverage [1].³ The interest in such adsorption isotherms has been further stimulated by the possibility of obtaining detailed information concerning the heterogeneity of a surface. The recent papers of Hill [2], Halsey [3], Rhodin [4], Halsey and Taylor [5], Sips [6], and Cook, Pack, and Oblad [7] indicate some promising approaches. It is believed that surface heterogeneities and impurities are the more common cause of the variable properties of commercial carbon adsorbents.

Nitrogen-adsorption measurements at relative pressures above 10^{-2} were reported by Deitz and Gleysteen [8] for a number of carbon adsorbents. As these samples were still available, the opportunity was taken to extend the data to relative pressures of about 10^{-7} . This corresponds to absolute pressures of about one-tenth micron of Hg.

2. Experimental Procedure

A four-stage McLeod gage,⁴ shown in figure 1, was added to a conventional adsorption apparatus. The calibration was made gravimetrically with mercury and by pressure-volume data, using helium. Pressures down to about 0.1 mm Hg could be measured with an accuracy of about 1 percent. An accuracy of

⁴ Acknowledgment is made to W. V. Loebenstein of the Surface Chemistry Section for the design and fabrication of this gage.

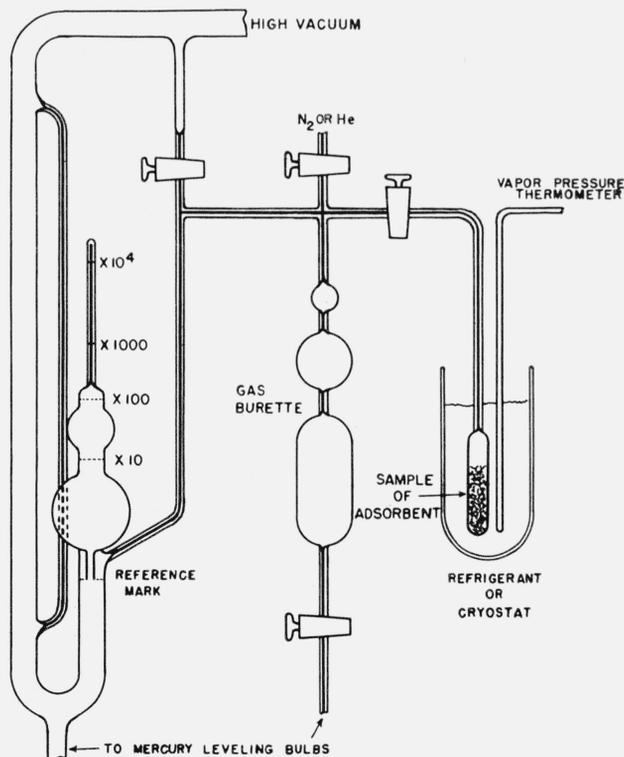


FIGURE 1. Diagrammatic sketch of the gas adsorption system.

¹ Research Associate of the National Bureau of Standards representing the Bone Char Research Project, Inc.

² Relative pressure is the ratio of the actual pressure of nitrogen to its equilibrium vapor pressure.

³ Figures in brackets indicate the literature references at the end of this paper.

2 percent was attained for pressures down to 10^{-2} mm Hg, 3 percent for pressures to 10^{-3} mm, and 5 percent or more for pressures as low as 10^{-4} mm, the lowest pressure attempted. The accuracy of the high-pressure (above 10 mm) readings was about 0.05 mm Hg.

Nitrogen from a cylinder of compressed gas (water-pumped) was purified by passage over copper at 350° C for the removal of residual oxygen and then through Ascarite and phosphorous pentoxide on glass cotton to remove carbon dioxide and water vapor.

The temperature of the bath surrounding the adsorption chamber was determined with either a nitrogen or oxygen vapor-pressure thermometer. The temperatures 90.0° and 77.7° K were obtained with liquid oxygen and liquid nitrogen, respectively, boiling at atmospheric pressure. The temperatures 72.2° and 69.5° K were obtained with a special cryostat described in the following paragraph. In all cases the temperature of the adsorption chamber was constant to within about 0.05° K.

2.1. Cryostat

The cryostat, see figure 2, consisted of a wide-mouthed 1-liter Dewar fitted with a rubber stopper and a 3.8-cm inside diameter brass tube closed at one end, that reached nearly to the bottom. Liquid nitrogen placed in the annular space between the brass tube and the Dewar was boiled under a fixed reduced pressure to obtain the desired temperature. In operation, air condensed inside the brass tube to form an excellent heat-transfer medium between the adsorption tube and brass tube. The vaporized nitrogen was drawn out of the cryostat through two 8-mm inside diameter tubes to a surge tank for smoothing pressure fluctuations.

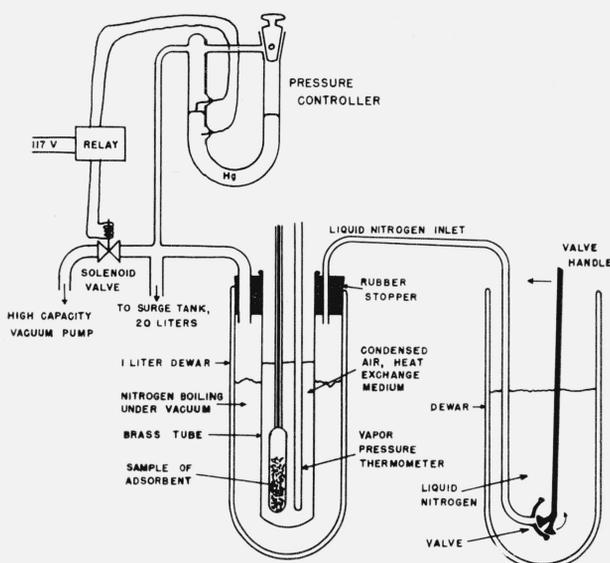


FIGURE 2. Diagrammatic sketch of the liquid-nitrogen cryostat and controls.

The pressure controller was similar to that used in vacuum distillations and consisted of a short mercury manometer with electrodes, as shown in figure 2. To start operations the stopcock on the controller was opened to the vacuum. When the desired operating pressure was reached, the stopcock was closed and the controller thereafter maintained this pressure. As a considerable volume of nitrogen was vaporized, the piping, solenoid valve, and the vacuum pump were adjusted to provide an adequate capacity. In operation, the solenoid valve cycled about once every 2 to 5 secs. Each opening of the valve brought a sudden pressure decrease, but with a sufficiently large surge tank these fluctuations resulted in variations of only about 5-mm Hg pressure over the liquid nitrogen in the cryostat. The slope of the vapor-pressure curve in the operating region is about 50 mm/deg, hence, the pressure variation corresponded to changes of only about 0.1° C. These fluctuations were smoothed by the heat capacity of the apparatus, and variations of only $\pm 0.05^{\circ}$ K were indicated by the vapor-pressure thermometer.

As a constant temperature was maintained over a number of hours, it was necessary to replenish the supply of liquid nitrogen in the cryostat. A valve designed to operate when immersed in liquid nitrogen is shown in figure 2. It consisted of a Pyrex ball joint without grease, with the tubing to the ball joint sealed off and extended out of the liquid, where it served as a handle. In the off-position the ball was almost disengaged from the socket. In this position the opening in the socket was effectively closed by the shoulder of the ball. To open the valve, the handle was twisted slightly to further disengage the joint. Despite minor leaks and infrequent clogging with ice crystals, the operation was quite satisfactory.

The entire cryostat was lagged except for a small window to observe the level of liquid nitrogen. About 3 liters of liquid nitrogen was consumed per hour in maintaining a constant temperature of about 70° K.

2.2. Corrections for Thermomolecular Diffusion

As there is an appreciable temperature difference between the manometer and the adsorbent, there is the possibility of introducing appreciable error from thermomolecular diffusion when measurements are made at very low absolute pressures. A careful review of the available literature was made [9,10,11,12], and the following equation of Liang [11] was considered the most appropriate for calculating the thermal transpiration factors:

$$R = \frac{P_1}{P_2} = \frac{\alpha_{\text{He}} (\Phi_g X)^2 + \beta_{\text{He}} (\Phi_g X) + R_m}{\alpha_{\text{He}} (\Phi_g X)^2 + \beta_{\text{He}} (\Phi_g X) + 1} \quad (1)$$

where P_2 is the observed pressure, P_1 the corrected pressure, and R the correction factor. X is the product of P_2 by d , where d is the diameter of the tube connecting the cold to the warm part of the apparatus. $R_m = (T_1/T_2)^{1/2}$, where T_1 = temperature of the

cold end of the connective tube (adsorbent temperature) and T_2 =temperature of the warm end of the connective tube (room temperature). The terms α_{He} and β_{He} are empirical constants: (1) $\alpha_{\text{He}}=2.52$ independent of temperature and (2) $\beta_{\text{He}}=7.68(1-R_m)$, the pressure being measured in millimeters of mercury and the tube diameter in millimeters. The factor Φ_g is the empirical relative "pressure-shifting factor" and is dependent upon the gas but not the temperature. It is related to the collision diameter of the gas molecules. With the above listed values of α and β , $\Phi_{\text{He}}=1$ and $\Phi_{\text{N}_2}=3.28$.

It is evident that as the pressure approaches zero ($X \rightarrow 0$); then R approaches its theoretical minimum value, R_m . Also, for high pressures (large values of X), R approaches unity. In the present work, the connecting tube was 1.0-mm diam, and nitrogen was the gas used at low pressures. In figure 3 are shown the variations of R with pressure for the present case in the interval from 0.0001 to 1 mm Hg for the four different temperatures. The values of R for pressures above 1 mm Hg are very close to unity.

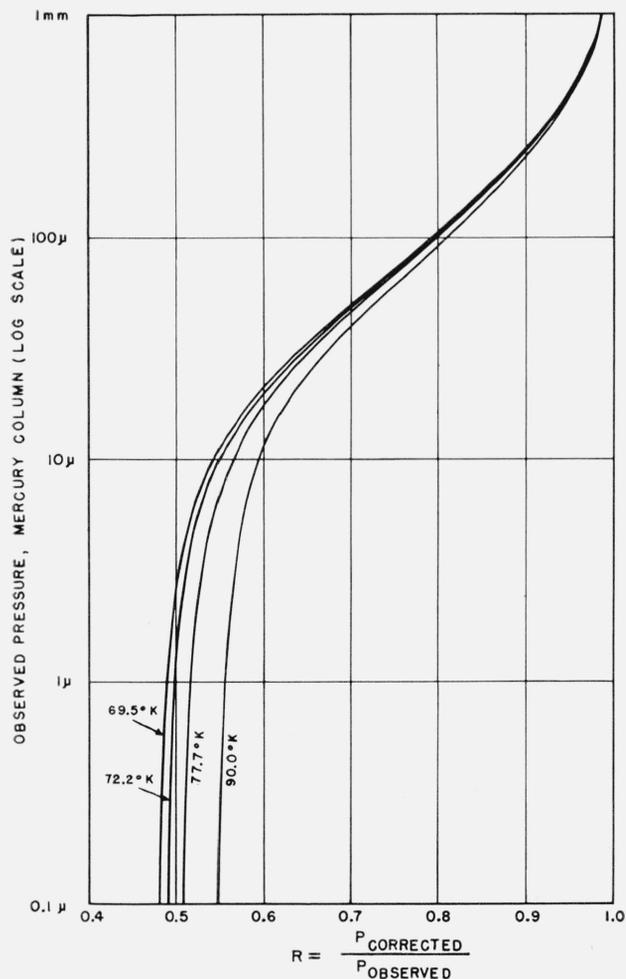


FIGURE 3. Thermal-transpiration factors for nitrogen in a 1.0-mm tube.

2.3. Materials

The three carbon adsorbents were among those previously investigated [8]. Char 2 was a new bone char obtained from the manufacturer. Char 27 had been employed in a cane-sugar refinery for a considerable time and had been removed from the char stock because of its high specific density (1.3 g/ml compared to 0.63 g/ml of char 2). The sample of char 27 used in this work differed from that previously reported [8] in that foreign substances visually detectable were mechanically removed. Char 1, an activated coconut-shell charcoal, was identical with that previously reported [8].

3. Experimental Procedure

The three adsorbents were simultaneously outgassed at 400° C for 16 hr at the beginning of the experiments. The pressure over the freshly outgassed adsorbent before any addition of nitrogen was always of the order of 10^{-6} mm Hg. In all cases, the first addition of nitrogen was very small, so that equilibrium was attained at a very low pressure. Then, more nitrogen was added, and the volumes adsorbed were obtained at increasing equilibrium pressures. After several points had been determined, the samples were outgassed for 16 hr at room temperature. This process of adsorption and outgassing at room temperature was repeated several times for each sample. Because of the great experimental difficulty in obtaining desorption data in the low pressure range, all of the results reported here are for adsorption.

4. Results

4.1. Attainment of Steady-State Pressure

The time required to reach a steady state was found to be a function of the final pressure of the adsorbed nitrogen, and depended also upon the stage of outgassing operations. After the first outgassing at 400° C, the steady state at the lowest pressure reading was attained in 1 to 2 hr, but in the measurements after the final outgassings at room temperature the attainment of a steady state required a much longer time, as is illustrated in figure 4. In all cases, the attainment of a steady state after the introduction of the first portion of nitrogen required the longest time. Curve A in figure 4 was observed for the lowest point of the isotherm for char 27 at 90° K (see fig. 6) and a steady-state pressure of 0.4 μ was realized after 10 hr. In several other similar cases it was observed that such a steady state persisted after 13 additional hr. Curve B of figure 4 illustrates that only 3 hr was required when the steady-state pressure was about 200 μ . When the pressure was in excess of 1 mm, the steady state was reached in about 20 min, in agreement with earlier experience [13] (curves C, D, E, and F, fig. 4).

The influence of consecutive outgassings on the quantity of nitrogen adsorbed was of particular interest. Figure 5 contains the low-pressure adsorp-

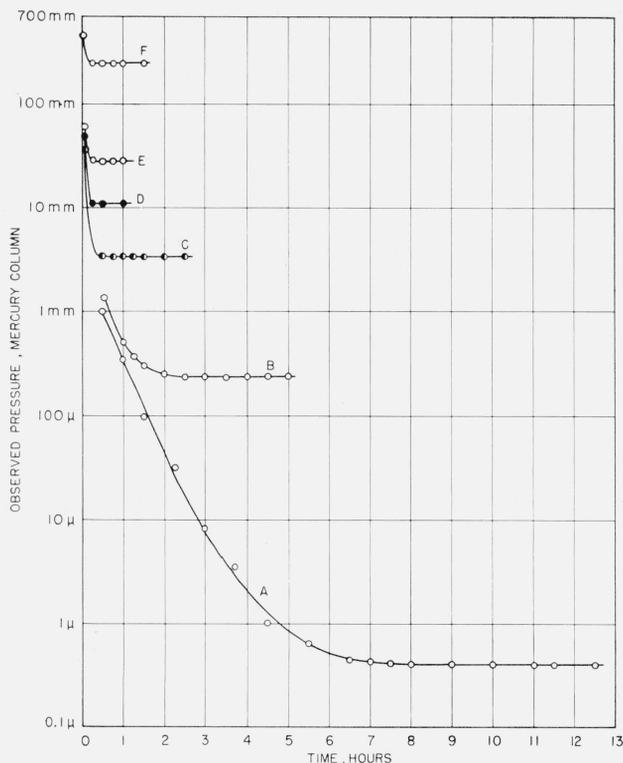


FIGURE 4. Attainment of steady state at various final pressures. Curves A and B: char 27 at 90° K; C, D, E, and F: char 27 at 72.2° K.

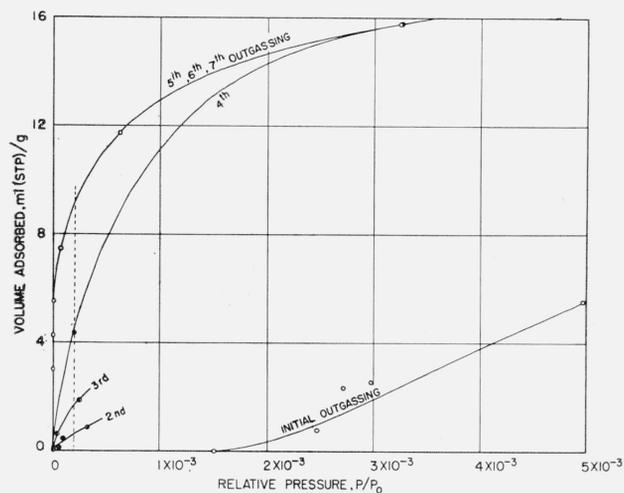


FIGURE 5. Low-pressure isotherms of nitrogen on char 2 at 90° K.

The influence of consecutive outgasings with the adsorbent at room temperature is shown; initial outgassing at 400° C.

tion data for char 2 at 90° K, and it may be seen from this example that the amount adsorbed increased with consecutive outgasings. By interpolating each curve to an equilibrium relative pressure of 2×10^{-4} , the volume of nitrogen (milliliter STP) adsorbed was 0.004 ml after the initial outgassing at 400° C and 0.65, 1.6, 4.3, 9.1, 9.1, and 9.1 ml, respectively, after each of six consecutive outgasings

TABLE 1. Adsorption of nitrogen on char 2

| 90.0° K | | 77.7° K | | 69.5° K | |
|------------------------------------|-------|-----------------------|-------|-----------------------|-------|
| p/p_0 | V | p/p_0 | V | p/p_0 | V |
| | ml | | ml | | ml |
| 1.63×10^{-7} | 3.00 | 1.28×10^{-7} | 3.60 | 6.72×10^{-6} | 9.05 |
| 1.23×10^{-6} | 4.25 | 2.21×10^{-6} | 6.23 | 5.33×10^{-5} | 11.76 |
| 5.63×10^{-6} | 5.50 | 2.05×10^{-5} | 8.69 | 3.27×10^{-4} | 14.80 |
| 6.33×10^{-5} | 7.44 | 2.67×10^{-4} | 11.16 | 5.26×10^{-3} | 21.48 |
| 6.22×10^{-4} | 11.76 | 3.09×10^{-4} | 12.60 | 1.87×10^{-2} | 24.63 |
| 3.25×10^{-3} | 15.77 | 6.97×10^{-4} | 14.71 | 4.18×10^{-2} | 27.00 |
| 0.0157 | 20.33 | 8.30×10^{-4} | 15.10 | 5.72×10^{-2} | 27.96 |
| .0519 | 24.15 | 2.54×10^{-3} | 17.96 | 9.63×10^{-2} | 30.22 |
| .0937 | 26.53 | 6.72×10^{-3} | 20.39 | 0.1215 | 31.69 |
| .1319 | 28.24 | 1.43×10^{-2} | 22.41 | .1634 | 33.40 |
| .1984 | 30.83 | 3.63×10^{-2} | 24.92 | .2197 | 35.95 |
| .2811 | 34.02 | 5.09×10^{-2} | 26.11 | .2725 | 38.36 |
| .3131 | 35.15 | 6.93×10^{-2} | 27.30 | .3493 | 42.15 |
| ----- | ----- | 9.14×10^{-2} | 29.10 | .4401 | 47.50 |
| ----- | ----- | 0.1323 | 30.41 | .5209 | 53.54 |
| ----- | ----- | .1785 | 32.38 | .6847 | 73.90 |
| ----- | ----- | .3942 | 41.70 | ----- | ----- |
| ----- | ----- | .5822 | 53.68 | ----- | ----- |
| $V_m = 25.54$ | | $V_m = 27.33$ | | $V_m = 28.65$ | |
| $p_0 = 2,698$ mm Hg | | $p_0 = 796.5$ mm Hg | | $p_0 = 270.3$ mm Hg | |
| V expressed at 273.16° K and 1 atm | | | | | |

TABLE 2. Adsorption of nitrogen on char 27

| 90.0° K | | 77.7° K | | 72.2° K | |
|-----------------------|-------|-----------------------|-------|-----------------------|-------|
| p/p_0 | V | p/p_0 | V | p/p_0 | V |
| | ml | | ml | | ml |
| 8.05×10^{-8} | 0.553 | 1.68×10^{-7} | 0.90 | 3.83×10^{-6} | 1.76 |
| 4.66×10^{-6} | 1.28 | 8.31×10^{-7} | 2.47 | 5.53×10^{-5} | 2.47 |
| 1.81×10^{-5} | 1.48 | 3.36×10^{-6} | 1.60 | 5.31×10^{-4} | 3.42 |
| 2.64×10^{-5} | 1.59 | 2.90×10^{-5} | 2.00 | 8.39×10^{-3} | 5.00 |
| 1.11×10^{-4} | 1.91 | 3.19×10^{-4} | 2.88 | 0.0272 | 5.81 |
| 3.20×10^{-4} | 2.19 | 4.67×10^{-4} | 3.01 | .0707 | 6.69 |
| 6.73×10^{-4} | 2.65 | 1.46×10^{-3} | 3.68 | .0920 | 7.03 |
| 9.87×10^{-4} | 2.95 | 4.23×10^{-3} | 4.31 | .1396 | 7.63 |
| 3.34×10^{-3} | 3.68 | 0.0153 | 5.16 | .1904 | 8.27 |
| 7.51×10^{-3} | 4.23 | .0362 | 5.80 | .3496 | 10.21 |
| 0.0116 | 4.54 | .0748 | 6.48 | .3982 | 10.82 |
| .0170 | 4.83 | .1481 | 7.40 | .5531 | 13.23 |
| .0232 | 5.08 | .2205 | 7.80 | .6162 | 14.47 |
| .0283 | 5.25 | .2945 | 8.57 | .6780 | 16.25 |
| .0331 | 5.38 | .3515 | 9.20 | .7774 | 20.39 |
| .0383 | 5.51 | .4194 | 9.96 | .8474 | 26.63 |
| .0445 | 5.65 | .5654 | 11.88 | .9212 | 39.53 |
| .0597 | 5.94 | .7934 | 17.69 | .9574 | 53.64 |
| .0923 | 6.43 | .8724 | 22.52 | ----- | ----- |
| .1147 | 6.69 | ----- | ----- | ----- | ----- |
| .1482 | 7.07 | ----- | ----- | ----- | ----- |
| .1979 | 7.60 | ----- | ----- | ----- | ----- |
| .2972 | 8.57 | ----- | ----- | ----- | ----- |
| .3075 | 8.79 | ----- | ----- | ----- | ----- |
| $V_m = 6.28$ | | $V_m = 6.60$ | | $V_m = 6.95$ | |
| $p_0 = 2,698$ mm Hg | | $p_0 = 796.5$ mm Hg | | $p_0 = 397.3$ mm Hg | |

at room temperature. The isotherms become coincident above a relative pressure of about 10^{-2} , in which region this effect was not evident.

In the first adsorption experiments with chars 2 and 27 after the first outgassing at 400° C, a small increase in pressure was observed in the system when the first portion of nitrogen at very low pressure was introduced into the adsorption chamber. This increase was observed only during the first few minutes

TABLE 3. Adsorption of nitrogen on char 1

| 90.0° K | | 77.7° K | |
|-----------------------|--------|-----------------------|--------|
| p/p_0 | V | p/p_0 | V |
| | ml | | ml |
| 7.23×10^{-7} | 31.37 | 3.46×10^{-7} | 31.37 |
| 1.5×10^{-5} | 66.48 | 2.95×10^{-5} | 106.36 |
| 6.7×10^{-5} | 101.60 | 9.26×10^{-5} | 141.88 |
| 1.74×10^{-4} | 135.59 | 2.30×10^{-4} | 178.05 |
| 3.51×10^{-4} | 161.07 | 4.19×10^{-4} | 201.22 |
| 5.33×10^{-4} | 174.41 | 8.67×10^{-4} | 223.06 |
| 6.8×10^{-4} | 181.64 | 1.50×10^{-3} | 235.86 |
| 2.7×10^{-3} | 220.81 | 2.40×10^{-3} | 246.65 |
| 5.2×10^{-3} | 242.34 | 2.79×10^{-3} | 251.05 |
| 7.9×10^{-3} | 252.34 | 7.12×10^{-3} | 270.59 |
| 0.0126 | 261.15 | 0.0173 | 293.73 |
| .0155 | 268.06 | .0254 | 304.91 |
| .0235 | 279.05 | .0412 | 320.04 |
| .0361 | 292.51 | .0482 | 325.16 |
| .0543 | 306.76 | .0585 | 331.40 |
| .0687 | 316.79 | .0744 | 339.06 |
| .0976 | 327.62 | .0835 | 342.73 |
| .1129 | 333.46 | .1332 | 354.35 |
| .1253 | 336.94 | .1773 | 360.39 |
| .1389 | 340.08 | .2431 | 364.88 |
| .1525 | 343.00 | .3219 | 370.68 |
| .1823 | 348.52 | .3552 | 372.24 |
| .2092 | 352.56 | .4097 | 374.98 |
| .2338 | 354.87 | .4651 | 376.95 |
| .2493 | 356.03 | .5084 | 378.78 |
| .2571 | 356.51 | .5316 | 379.58 |
| .2592 | 356.87 | .6317 | 383.84 |
| .2627 | 357.29 | .6897 | 386.50 |
| .3387 | 364.20 | .7136 | 387.20 |
| .3699 | 373.16 | .7662 | 387.44 |
| ----- | ----- | .7672 | 390.61 |
| ----- | ----- | .8241 | 393.46 |
| ----- | ----- | .8290 | 394.59 |
| ----- | ----- | .8377 | 395.58 |
| ----- | ----- | .8743 | 399.78 |
| ----- | ----- | .9282 | 402.54 |
| ----- | ----- | .9328 | 405.47 |
| ----- | ----- | .9687 | 410.45 |
| ----- | ----- | .9810 | 420.91 |
| ----- | ----- | .9880 | 431.76 |
| ----- | ----- | .9996 | 471.56 |
| $V_m = 378$ | | $V_m = 397$ | |
| $p_0 = 2,698$ mm Hg | | $p_0 = 796.5$ mm Hg | |

of contact, and then the pressure decreased in a normal way toward equilibrium. When this effect was observed, the final values of the relative pressures were notably high. A possible explanation is presented in a later paragraph.

The times required to realize a steady state for char 27 were only about half those required for chars 2 and 1 at the same final pressure. Periods of about 50 hr were necessary to attain equilibrium in chars 1 and 2 at the lowest pressures obtained.

The volumes of nitrogen adsorbed for char 2 (69.5° , 77.7° , 90.0° K), char 27 (72.2° , 77.7° , 90.0° K), and char 1 (77.7° , 90.0° K) are given in tables 1, 2, and 3, respectively. The data recorded are the final steady-state values observed after a number of consecutive outgasings at room temperatures sufficient to yield reproducible values for the volumes of nitrogen adsorbed.

4.2. Calculation of Isotherm Equation

An isotherm equation was sought, valid for the region of the lowest measurable pressures, which could then be used with some confidence to extrapolate to the volume adsorbed at pressures too low to measure. Such an extrapolation is necessary in the calculation of thermodynamic functions of adsorbed molecules [14].

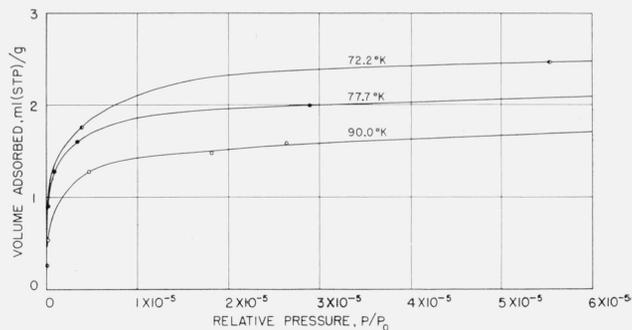
Plots of the volume adsorbed as a function of relative pressure for chars 2, 27, and 1 yielded curves that became steeper as the pressure was reduced, as shown in figure 6 for char 27. A linear behavior was found, however, on a Freundlich plot for all temperatures and all chars from the lowest relative pressures up to about 10^{-4} . Typical plots are shown in figure 7. The isotherms observed at the lower temperatures were linear up to a higher value of relative pressure. For example, in char 27 at 72.2° K a straight line was observed up to $p/p_0 \cong 3 \times 10^{-2}$; at 77.7° K the straight line was valid up to 5×10^{-4} , and at 90.0° K up to 4×10^{-4} . A similar behavior was observed in chars 1 and 2. Parameters n of the Freundlich equation were determined, and these are given in table 4.

TABLE 4. Isotherm constants for adsorption of nitrogen

| Char | Temperature | Freundlich constant, n | B.E.T. parameters | | | |
|------|-------------|--------------------------|-------------------|-----|-------|--------------|
| | | | V_m | c | F^a | Surface area |
| | $^\circ K$ | | ml | | | m^2/g |
| 1 | 77.7 | 3.92 | 397 ^b | 46 | 4.383 | 1,744 |
| | 90.0 | 3.82 | 378 ^b | 65 | 4.601 | 1,741 |
| 2 | 69.5 | 7.75 | 28.65 | 194 | 4.255 | 121.9 |
| | 77.7 | 7.39 | 27.33 | 189 | 4.383 | 119.8 |
| | 90.0 | 7.31 | 25.54 | 183 | 4.601 | 117.5 |
| 27 | 72.2 | 7.30 | 6.95 | 110 | 4.295 | 29.85 |
| | 77.7 | 7.30 | 6.60 | 123 | 4.383 | 28.93 |
| | 90.0 | 7.30 | 6.28 | 107 | 4.601 | 28.89 |

^a Packing constant based on density of liquid nitrogen for converting V_m to surface area.

^b Calculated from the Langmuir isotherm.

FIGURE 6. Nitrogen adsorption isotherms on char 27 at 72.2° , 77.7° , and 90.0° K.

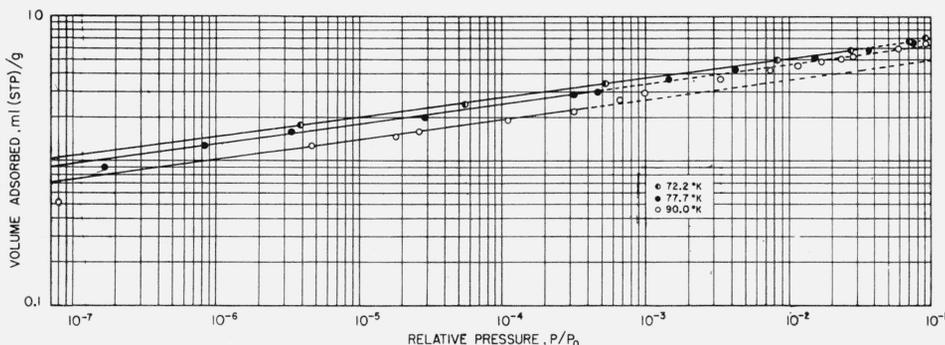


FIGURE 7. *Freundlich isotherms for the nitrogen adsorption data at low pressure on char 27 at 72.2°, 77.6°, and 90° K. Both scales are logarithmic.*

4.3. Surface Area Calculations

The adsorption data for chars 2 and 27 were found to give linear B. E. T. plots in the range of relative pressures between 0.05 and 0.35. The values of V_m and c were evaluated from the B. E. T. equation for a free surface

$$\frac{p}{V(p_0 - p)} = \frac{1}{cV_m} + \frac{c-1}{cV_m} p/p_0, \quad (2)$$

where V (reported at STP) is the volume adsorbed at pressure p , and p_0 is the saturation pressure. The values of the constants V_m and c are given in table 4. The corresponding surface areas were based on a packing factor calculated from the density of liquid nitrogen [8]. The values given in table 4 were calculated from the adsorption data recorded in tables 1, 2, and 3. V_m , also calculated from the data obtained in the first adsorption run after outgassing at 400° C, was found to be 26.5 compared to 25.5 for the steady-state value. Despite the large difference between the first portion of this isotherm and the corresponding part of the isotherm obtained after several outgasings at room temperature, there was close agreement in the values of V_m obtained from the two sets of data.

The adsorption data for char 1 did not give a linear B. E. T. plot. The correct values of V_m for char 1 are given by Langmuir plots, which were found valid in the relative pressure range between 0.2 and 0.8. The values of V_m at 77.7° and 90.0° K are also given in table 4.

5. Discussion

5.1. Attainment of Steady-State Pressures

As the carbon adsorbents investigated were essentially pyrolysis residues of bone or coconut shell and not subject to a defined state of decomposition, it is highly probable that some surface complex containing carbon, hydrogen, and oxygen remained with the adsorbent. This could decompose into

CO₂, CO, and H₂ by continued thermal treatment. Some of this complex could be removed during the outgassing at 400° C, but an appreciable portion always remained in the adsorbent. The presence of this residual complex could have a major influence on the observed steady-state pressure in the range of very low pressures.

The experimental results suggest that one of the factors responsible for the behavior observed at low pressures may be directly related to the residual complex. The first portion of nitrogen introduced was able to displace some constituent of the complex, and, as a result, the liberated decomposition products, such as CO, CO₂, and H₂, contributed to the observed pressure. Unfortunately, means were not available to analyze the products of outgassing at the low pressures employed, but this would be a desirable future experiment. The consecutive outgasings at room temperature, together with introduction of more nitrogen, served to remove the complex until a stage of relative stability was reached, as shown by the final reproducible values. The particular program of outgassing is obviously one of a possible large number. Any alteration in the technique of outgassing, such as a second heating to 400° C, would no doubt have had an additional influence on the number of adsorption sites shared between the surface complex and the adsorbed nitrogen.

Another factor of influence is associated with the diffusion of gas molecules at low pressures. Because of the intricate structure of the porous material, more time is required for the nitrogen to locate the adsorption sites of minimum potential energy. A similar argument may be valid in connection with surface-diffusion phenomena. Some such consideration is required to explain the fact that even relatively well outgassed adsorbents (400° C for 16 hr) required long periods to attain equilibrium in the low-pressure range [15].

Other things being equal, relatively shorter periods were required to attain a steady state for char 27 compared to char 2. It has been shown elsewhere [16] that the crystalline structure of basic calcium phosphate (about 90 percent in these materials) was

more highly developed in char 27. In this case the contribution of the voids in the porous structure to the total adsorbing surface was less. In addition, the carbonaceous residue in char 27 had a greater stability as a result of many heatings to which it had been subjected in the commercial revivification process.

5.2. Validity of Isotherm at Very Low Pressures

The experimental data show that a Freundlich isotherm is valid in the measurable range at very low pressures. When a Langmuir isotherm is valid at low pressures, Henry's law, $V=ax$, is automatically obtained as the limiting case. Hill [17] has shown from statistical mechanical-thermodynamic considerations that all adsorption isotherms must approach Henry's law. Hence, in the present case where Freundlich isotherms are observed at the lowest pressures, it is necessary to postulate a transition range below which one must realize the linear dependence of adsorbed volume on pressure. It is not known where this range exists for the adsorbents investigated.

For Henry's law to be obeyed, the slope of the plots in figure 7 must be unity. It may be seen from these graphs that the first observed points at the lowest pressure for the isotherms at 90.0° and 77.7° K are displaced in the correct direction. However, it will be necessary to obtain additional data at even lower pressure to be sure of this behavior.

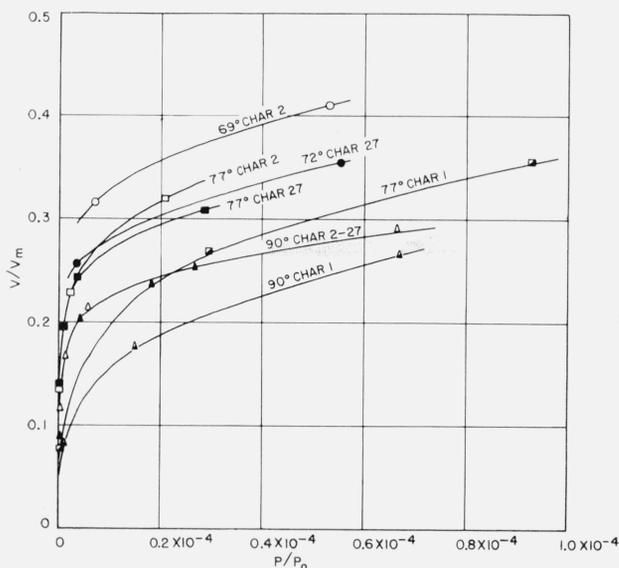


FIGURE 8. Low-pressure adsorption data for char 27 at 72.2°, 77.7°, and 90° K.

The ratio, v/x , is shown as a function of x , where x =relative pressure, and v =volume of nitrogen adsorbed (STP).

5.3. Surface Area

When the ratio V/V_m was plotted (see fig. 8) as a function of p/p_0 from 10^{-7} to 10^{-4} , it was found that the curves for chars 2 and 27 were in coincidence at 90° K. In this region no more than 40 percent of the surface was covered. This agreed with previous work in the range 0.1 to 0.3 [8], where the entire surface was covered. However, at the lower temperatures, the curves for different adsorbents were separated to a significant extent, which implies a different interaction of the nitrogen molecules with the surface. For the case of a given adsorbent at 2 or 3 temperatures, the curves were separated to greater extents than indicated by the corresponding changes in the densities of liquid nitrogen. The values of V/V_m are largest at the lowest temperature for a given value of p/p_0 .

The surface areas given in table 4 indicate an increase with decrease in the temperature. It is not known whether or not this is within the experimental error of the V_m determination. It may also be related either with unknown changes in density of the adsorbed nitrogen phase or with the possibility that the effective van der Waal's diameter of the adsorbed nitrogen molecule at the different temperatures is critical with the dimensions of the voids. Therefore, the surface available to a nitrogen molecule, especially in porous materials, might be correspondingly greater.

5.4. Conclusions

The attainment of equilibrium at very low pressures is a complicated process, in which the nature of the surface and the impurities associated with the solid surface play an important role. Variations in the outgassing techniques can change this part of the isotherm to a notable extent.

As the nature of the predominant forces responsible for adsorption changes significantly with surface coverage, no known isotherm equation can be expected to be valid from $x=0$ to $x=1$. The Freundlich equation appears to be valid at very low pressures in a great many cases, but it is not valid when the surface coverage approaches a monolayer where x is approximately 0.1. The B.E.T. equation appears to be frequently valid between the point where the Freundlich relationship fails and relative pressures of about 0.35. In this region (0.05 to 0.35) the factors that are not taken into account in the B.E.T. model would not contribute appreciably to the volume adsorbed. The behavior above 0.35 in relative pressure has at present no adequate theoretical basis. In general, one can say that the nature of the predominant forces involved in any adsorption process is a function not only of the nature of the adsorbate, adsorbent, and temperature, but also of the pressure range, which determines the fraction of the surface covered.

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