Water was removed through a Dean-Stark trap. Crude material was washed with ~ 1*M* NaOH, dried with anhydrous K_2CO_3, and distilled at reduced pressure under a nitrogen atmosphere. Middle cuts free of carbonyl and hydroxyl absorption in the IR were used for analyses. Crude yields were nearly quantitative. Purified material was obtained in 60 to 90% yield and stored under nitrogen.

Compounds of Type III were usually made according to a modified procedure of Fieser (*9*). One-half mole each of aldehyde and 1,2-ethanedithiol were mixed in 300 ml. of glacial acetic acid. Five milliliters of BF_3 in ether (Eastman Organic Purified) was added with stirring. An exothermic reaction occurred. After cooling, methanol was added. A small piece of dry ice induced crystallization if the product was a solid. The product was recrystallized from methanol or sublimed in vacuo. Yields of purified product were 60 to 80%. Melting points are uncorrected. Compounds of Type III were not prepared by this procedure owing to polymer formation.

Density and Refractive Index. Density measurements were made in new water-calibrated, 1-ml. volumetric flasks. Refractive index was measured on a Bausch & Lomb refractometer, Type 33-45-58, with prisms thermostated at 20° C.

Spectra. All IR spectra reported were taken on a Perkin-Elmer Model 21. Bands reported in Table II are medium to strong intensity and broad. Complete spectra were taken between 2 and 15.5 microns (5000 to 645 $cm.^{-1}$), and characteristic absorptions where appropriate were noted at expected wavelengths (phenyl, nitro, etc.). The absence of carbonyl absorption at 5.6 to 6.0 microns (1788 to 1667 $cm.^{-1}$) was used as an indication of sample purity.

NMR spectra were taken with a Varian A60 operating at 60 mc. per second. Chemical shifts are recorded on the scale relative to an internal tetramethylsilane reference. The sweep width used was 500 c.p.s.

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Low Pressure Adsorption of Helium on Microporous Solids

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The adsorption of helium on five different microporous solids was measured by a gravimetric technique over a temperature range from boiling nitrogen to room temperature, at pressures at and below 1 atm. (absolute). The procedure is detailed, and the results are presented. The results compare favorably with some other published findings.

THIS WORK was undertaken in an attempt to establish the existence or absence of measurable amounts of helium adsorption on various representative microporous solids. Helium adsorption is negligibly small, and an assumption to this effect has an important utility in the measuring of adsorption of other gases. A similar assumption also has a use in establishing mechanisms of flow through microporous materials. The error accompanying this assumption in the latter determination may be significant (*5*), and principally for this reason, the work was undertaken.

Since zero helium adsorption could not be assumed in the present case and since gravimetric measurements were to be made, an alternate method of evaluating the volume occupied by the solid material had to be used to assess the value of buoyancy. Buoyancy determinations were of extreme importance in this work since the magnitude of the buoyant force was several times that of the weight of gas adsorbed in the usual case. Thus, the otherwise minor uncertainties in solid volume could lead to major uncertainties in the amount of gas adsorbed. Although several methods of determining the solid volumes were considered, the one used in this investigation was that of measuring the apparent weight change upon immersion of the sample (including its container) in liquid nitrogen.

Adsorption isotherms of nitrogen and argon were measured for purposes of comparison, and surface areas of the adsorbents were determined from nitrogen adsorption at the temperature of its normal boiling point.

EXPERIMENTAL

Adsorbents. There were five different adsorbents used in this work.

GRADE KH-1 ACTIVATED CHARCOAL, approximately

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8-mesh (Barneby-Cheney Co., Ohio), is referred to as KH-1.

GRADE SXC ACTIVATED CARBON, approximately 6-mesh (Columbia Chemicals Co., Pittsburgh, Pa.), is referred to as SXC.

MOLECULAR SIEVES, TYPE 13X has pore diameters of approximately 9 A. and is referred to as 13X Sieve.

MOLECULAR SIEVES, TYPE 5A has pore diameters of approximately 5 A. and is referred to as 5A Sieve.

MOLECULAR SIEVES, TYPE 4A has pore diameters of approximately 4 A. and is referred to as 4A Sieve.

All of the Molecular Sieves samples were donated by the Linde Co., Division of Union Carbide Co., Tonawanda, N.Y. The material consisted of cylindrical particles, $\frac{1}{16}$-inch in diameter and $\frac{1}{8}$- to $\frac{5}{16}$-inch long.

Adsorbates. The adsorbates investigated were helium, nitrogen, and argon which were procured from the Matheson Co., East Rutherford, N.J. The nitrogen was the Prepurified grade, the helium and argon grades were unspecified. Prior to use in adsorption measurements, the helium was passed through a bed of activated carbon cooled by a liquid nitrogen bath. The nitrogen and argon adsorbates were similarly pretreated except the cold bath was a dry ice–acetone mixture. During the course of the work it was observed that cold bath pretreatment resulted in a noticeable residue of water in the trap.

Apparatus. The principle component of the apparatus used in this investigation was a balance mechanism obtained from the Cahn Instrument Co., Paramount, Calif. The balance was a Model 1501 with electronic power supply, the housing was a Cahn Instrument Co. No. 1507 Glass Vacuum Bottle Accessory of borosilicate glass.

The sample was enclosed in a tube constructed of approximately 40-mm. O.D. 96% silica glass (Vycor) tubing at the bottom, a graded seal, and borosilicate glass at the top. The sample enclosure tube had a total length of about 20 inches. The adsorbent sample was contained in a small bucket made of aluminum foil, and this was suspended from the balance on a Nichrome wire 0.004 inch in diameter. The sample was suspended from a position on the beam such that its distance from the pivot was one-fifth of the length of the counterweight lever arm. A schematic diagram of the apparatus is shown in Figure 1.

The principal supporting equipment included: a cold cathode ionization gage, Model No. 100-A, manufactured by Miller Laboratories, Latham, N.Y.; a "Standard Clean-Out" 50-inch manometer manufactured by the Meriam Instrument Co.; a VMF-10 oil diffusion pump with a Welch Duo-Seal Model 1300 mechanical fore pump. Additionally, a degassing furnace was made by wrapping Nichrome wire around an Alundum tube approximately 2½ inches I.D. by approximately ¼-inch wall by 14 inches long. At a voltage of 110 v., this heater dissipated somewhat more than 600 watts. The Alundum tube was sealed at the bottom with refractory cement and was placed inside a sheet metal container about 8 inches in diameter. Vermiculite was packed between the core and the container walls, and the annulus at the top was sealed over with refractory cement. Power to the furnace was regulated by a variable auto-transformer. The furnace was commonly operated at 50 volts and below.

Sample Preparation and Weighing. A quantity of adsorbent amounting to 600 to 1000 mg. was degassed in place by simultaneous evacuation and heating. The temperature was raised slowly in three increments to a maximum of about 300° C. over the course of about two days.

During the latter stages of heating, the vacuum gage was turned on. Pressures indicated were commonly about 0.3 micron.

Rapid temperature rises resulted in a brown coloration on the lighter colored samples. This was taken to indicate a decomposition of organic matter prior to boil off. At any rate, the slow temperature rise eliminated the discoloration and was also used on the carbon samples although, of course, there were no visual effects.

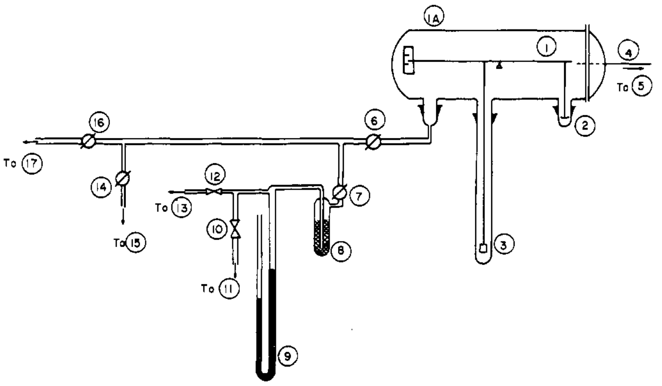

Figure 1. Gravimetric adsorption apparatus

1. Balance mechanism, 1A balance housing
2. Counterweight
3. Adsorbent sample
4. Balance control cable
5. Balance controller
6. Stopcock
7. Stopcock
8. Carbon trap
9. Mercury manometer
10. Purge pump valve
11. Purge pump (for purging gas sample inlet system)
12. Gas sample valve
13. Gas supply
14. Stopcock
15. Vacuum gage
16. Stopcock
17. Main vacuum pumping system (for degassing adsorbent sample)

When a condition of constant weight prevailed, the actual degassed weight of the sample was determined by taking into account the amount of counterweight on the balance, the weights of the counterweight and the sample suspension systems, and the reading of the balance.

As was usually the case, the counterweight had to be changed at this point to enable weighing on the most sensitive scale of the balance (0 to 5 mg.). That is, the counterweight had to less than compensate for the sample, but yet be close enough to total compensation that the difference would be less than 5 mg.

To adjust the counterweight, it was necessary to open the system. However, if a helium atmosphere were maintained around the sample and the furnace left in place, subsequent re-evacuation and desorption could be accomplished in 2 hours or less.

Helium Adsorption Measurements. With the adsorbent sample hot and degassed, helium was admitted through a carbon trap chilled with liquid nitrogen into the apparatus to a pressure of about one atmosphere. The desired temperature control bath was placed around the sample enclosure tube in place of the furnace and measurements were begun. A measurement actually consisted only of reading the pressure on the manometer and reading the balance. The time required for apparent equilibrium was fairly short, depending on the temperature and the adsorbent. Usually five minutes were allowed for equilibrium to prevail, in some instances, 15 minutes were allowed.

Following the completion of a measurement, the pressure was changed, either raised by admitting more gas or lowered by removing gas with a purge pump, and another measurement was made. Pressures were maintained between 0.2 and 1.6 atm. (absolute). The increments of pressure change were usually 0.2 to 0.3 atm. From the pressures and balance readings, a value for balance deflection per unit pressure was determined and used as described later.

When an apparently satisfactory coverage of the pressure range was completed, a different temperature bath was placed around the sample enclosure tube and a similar set of measurements was made. This procedure was repeated for all the temperatures used.

Nitrogen and Argon Adsorption Measurements. The adsorption of nitrogen and argon was measured at various temperatures in conjunction with this work in an effort to establish comparisons and, in the case of nitrogen at its atmospheric boiling point, to determine the adsorbent areas by the Brunauer, Emmett, Teller (*1*) (B.E.T.) method. All of the measurements with these two gases were made in a more conventional manner, starting with an evacuated system and raising the pressure in small increments, making a measurement at each of the pressures. A much longer time was required to attain equilibrium with these gases.

The helium adsorption measurements previously described were done in a different manner because it was observed that with the adsorbent sample cooled and a high vacuum prevailing, an increase in sample weight occurred with time. Further, the increase was quite large compared with changes anticipated in the course of measuring helium adsorption. This weight change, which was believed to be caused by contamination from stopcock grease vapors, could be diminished by as much as a factor of 100 or more by the introduction of a slight gas pressure. Hence, in the helium work, the sample was never cooled without there being at least a quarter of an atmosphere of helium present in the weighing chamber.

Liquid Immersion. To obtain a measured value of the volume of the solid sample, the sample and its container were immersed in a liquid and weighed under those circumstances. From the change in weight upon immersion in the liquid, and the density of the liquid, the volume of the sample container with sample was determined.

Nitrogen could easily and quickly be condensed in the sample enclosure tube, so in general, liquid nitrogen was used as the immersing liquid. The measurement was made immediately following the nitrogen adsorption measurements at liquid nitrogen temperatures by increasing the adsorbate pressure to about 1.5 atm. and holding until nitrogen had condensed in the tube to such a depth that it covered the sample.

With the sample immersed in liquid nitrogen, the apparent weight was determined. The authors assumed that all the void spaces of the adsorbent were filled with liquid nitrogen.

Apparently the pores of the 4A sieves were too small for appreciable nitrogen entry at liquid nitrogen temperature, and therefore this adsorbent was immersed in water. To accomplish this, water was placed in a container which was connected in place of the vacuum gage and was heated slightly after being opened to the evacuated system. Condensation in the sample enclosure tube was accomplished with an ice bath.

Methods of Temperature Control. Temperatures were controlled around the sample by surrounding the sample enclosure tube with an appropriate bath contained in a Dewar flask. Various materials were used in an effort to maintain an approximately constant temperature. A tabulation is presented below:

Temperature		
° C.	° K.	Bath
−195.8	77.4	Boiling nitrogen
−130	143*	Frozen *n*-pentane
−95	178*	Frozen methanol
−78.5	194.7	Solid CO_2 in methanol
−40	233*	Water-isopropanol slush
−20	253*	Water-ethylene glycol slush
0	273.2	Water-ice
+25	298	Tap water

Temperatures marked with an asterisk (*) were only approximate and had to be measured in each case because concentration changes caused variations in the freezing points. These temperatures were measured with a calibrated thermocouple. The temperature of the tap water bath was measured with a −10° to 100° C. mercury in glass thermometer (0.2° graduations).

Most of these baths were of course not truly isothermal. However, the heating load was normally very small and measurements showed that temperatures rarely changed by as much as 0.2° C. and never more than 0.5° C. during the course of the adsorption isotherm measurement.

The thermocouple calibration was performed by immersion in boiling nitrogen, boiling oxygen, solid CO_2 in methanol, and a solid-liquid mixture of *n*-pentane. A correction curve was constructed whereby the deviation of the thermocouple EMF from published tables could be read as a function of the indicated EMF. During the calibration, corrections for the barometric pressure were made on the boiling points of nitrogen and oxygen.

RESULTS

The complete results of this work have been presented in voluminous detail by Springer (*7*). A summary of the findings is presented in Figures 2, 3, and 4 and Table I.

The scatter of the helium adsorption data is evident in Figures 2 and 3. While the curves shown represent least-squares straight-line fits of the individual collections of data for various adsorbents, apparently one could as well represent all of the carbon data and all of the molecular sieves data as if both carbons and all three sieves were equivalent (Figure 3).

Figure 3 also shows data for nitrogen and argon adsorption on the 13X sieves. These are presented for purposes

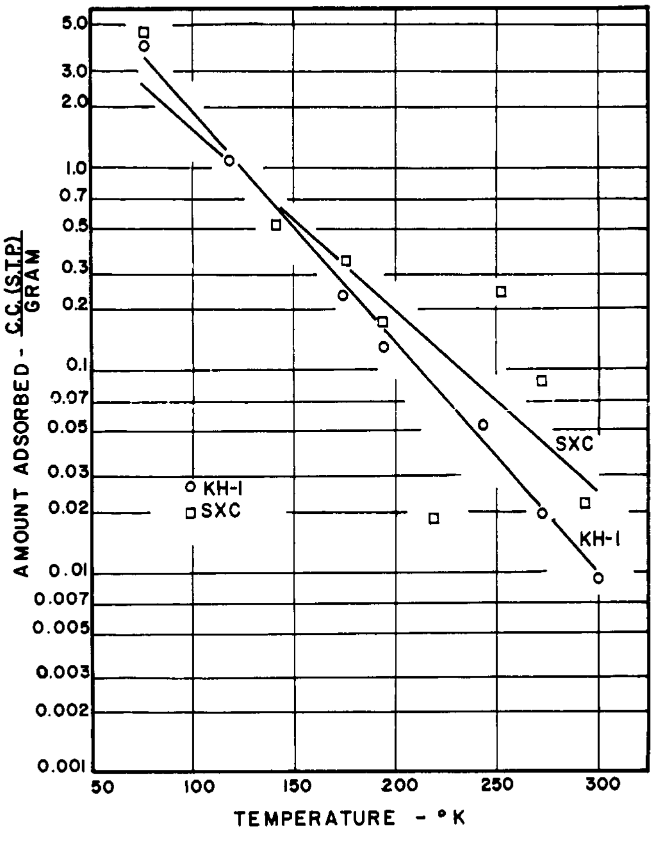

Figure 2. Helium adsorption on carbons at 1.0 atm. (absolute)

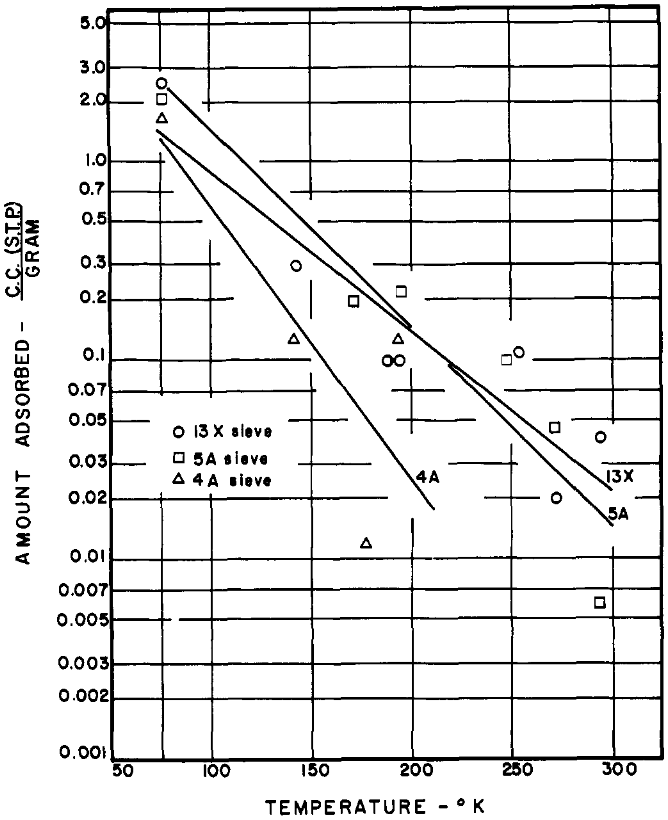

Figure 3. Helium adsorption on molecular sieves at 1.0 atm. (absolute)

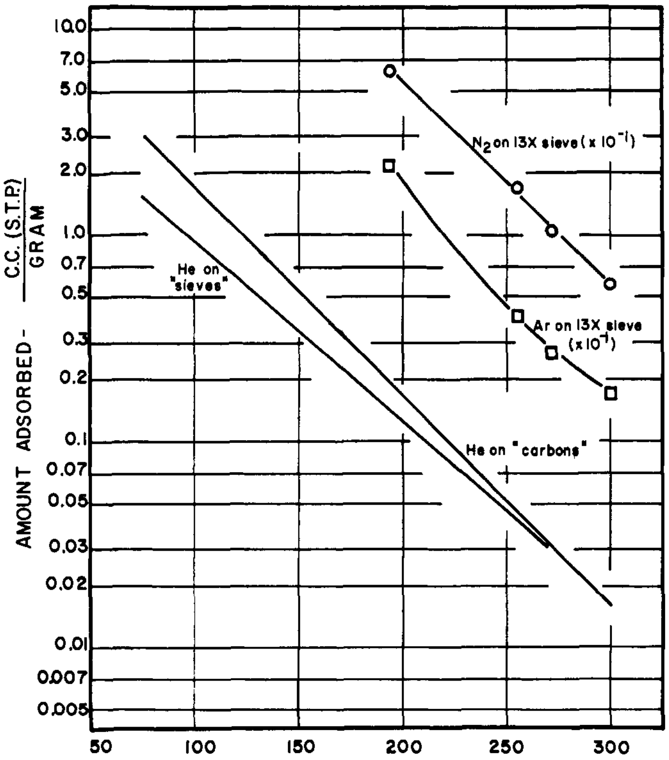

Figure 4. Generalized helium adsorption isobars on carbons and on sieves.

Nitrogen and argon isobars are also shown for comparision for 13X sieve. Pressure in oll cases is 1.0 atm. (absolute)

Table I. Helium Adsorption at 1.0 Atm.

Temp., °K.	Amount Adsorbed, Cc. (S.T.P.)/Gram
4A Sieves[a,b]	
77.4	1.73
142.9	0.13
177.8	0.012
194.7	0.13
5A Sieves[c]	
77.4	2.14
173.4	0.20
194.7	0.22
246.9	0.10
273.2	0.045
294.8	0.006
13X Sieves[d]	
77.4	2.57
143.4	0.30
187.6	0.10
194.7	0.10
254.6	0.11
273.2	0.02
296.4	0.04
KH-1 Carbon[e]	
77.4	3.92
118.2	1.07
175.3	0.23
194.7	0.13
244.0	0.053
273.2	0.019
302.8	0.009
SXC Carbon[f]	
77.4	4.60
140.8	0.51
177.4	0.34
194.7	0.17
219.1	0.018
253.7	0.24
273.2	0.087
294.5	0.921

[a] Surface area of adsorbent, 592 sq. meters/gram determined from plot of Langmuir equation using nitrogen adsorption at 194.7° K. [b] V_m/a (volume adsorbed in a monolayer per unit area) was determined for 194.7° K. by comparing $\underline{V}_m$ at 194.7° K. with $\underline{V}_m$ at 77.4° K. for the 5A sieves. Such a determination was necessary because the internal surfaces of the 4A sieves were not accessible to nitrogen at 77.4° K. See also (2). [c] Surface area of adsorbent, 691 sq. meters/gram determined by the method of Brunauer, Emmett, and Teller (B.E.T.) using nitrogen adsorption at 77.4° K. [d] Surface area of adsorbent, 692 sq. meters/gram determined by B.E.T. method using nitrogen adsorption at 77.4° K. [e] Surface area of adsorbent, 2027 sq. meters/gram determined by B.E.T. method using nitrogen at 77.4° K. [f] Surface area of adsorbent, 1670 sq. meters/gram determined by B.E.T. method using nitrogen adsorption at 77.4° K.

of comparison, since the 13X sieves were rather typical of all the adsorbents.

These data are for adsorption at 1.0 atm. (absolute) in all cases. Such a presentation arises from the method of obtaining the adsorption data.

From the measurements made with helium as the adsorbate, a value for balance deflection per unit pressure (ΔR) was obtained. This value was constant for any given adsorbent at any given temperature. By applying an appropriate conversion factor (balance calibration, C) a value of apparent mass change of the adsorbent sample per unit pressure (ΔM) was reached (except at the lowest temperature—i.e., 77.4° K.—the apparent mass change per unit pressure was negative). By assuming ideal behavior of helium, a buoyancy correction, B, was calculated, which was then added to ΔM.

Thus,

$$\Delta M = C(\Delta R)$$

and

$$A = P(\Delta M) + B$$

where

C = balance calibration, mg./balance scale division
ΔR = change in balance reading per unit pressure, divisions/atm.
ΔM = apparent change in mass per unit pressure, mg./atm.
P = aboslute pressure, atm. (P was taken as 1.0 atm.)
B = $V_s \rho_g$
V_s = volume of solid, cc.
ρ_g = density of gas at 1.0 atm. (abs.), mg./cc.
A = mass of gas adsorbed, mg.

The value of A, then, was the measured amount adsorbed on the sample at a pressure of 1.0 atm. (absolute). The value A was then converted to cubic centimeters (S.T.P.) per gram of adsorbent.

Obviously the above method was inappropriate for nitrogen and argon adsorption since the adsorption isotherms were not straight lines for these gases. Rather, for plotting Figure 3, values were taken from conventional isotherm plots (*7*).

DISCUSSION

Precision of Results. The apparent precision of the foregoing results leaves much to be desired. On the other hand, part of the scatter evident is the natural result of the necessity of making a buoyancy correction which is obviously large relative to the total measurement. While the lower temperature values, in general, are probably more nearly valid than those at the higher temperatures, no attempt was made to give added weighting to the lower temperature results.

A reliable estimate of probable error in this work would be difficult to ascertain. The balance provided weight change measurements to a precision of about ±0.5 μg., which, in consideration of the usual sample size, was approximately equivalent to ±0.004 cc. (S.T.P.) per gram of adsorbent. However, there are other uncertainties, not so easily determined.

The values used for solid volume were those obtained by immersion in liquid nitrogen. Obviously the volume of the solid when immersed in liquid nitrogen is not the same as when immersed in gaseous helium. An approximation of the true solid volume can be made as being the measured volume less the product of the absorbent area times one-half of the mean diameter of the adsorbate molecules, thus accounting for a volume adjacent to the solid surface which is unoccupied by adsorbate.

Applying such a correction to the charcoal volumes in this work shows that the solid volumes may be of the order of 0.1 cc. per gram less than the volume measured. Helium, however, also leaves an unoccupied volume adjacent to the surface which may be of the order of 0.07 cc. per gram. When these corrections are combined, the volume of solid relative to the helium becomes approximately 0.03 cc. per gram less than the volume measured in liquid nitrogen, subsequently yielding lower amounts adsorbed after data reduction. The difference in amounts adsorbed when accounting for the unoccupied volume range from 0.1 to 0.02 cc. (S.T.P.) per gram of adsorbent from the lower temperatures to the higher temperatures respectively. In some instances the values for amount adsorbed become negative, a situation not uncommon when considerable scatter occurs in results near zero, but which also gives rise to doubts regarding the accuracy of the corrections employed.

No correction for the change in solid volume with temperature was attempted. Initially it would be presumed that increased solid volume from thermal expansion would result in the indication of greater amounts adsorbed. However, the possibility of a widening of cracks and other inaccessible micropores along with an increased mobility of adsorbate makes conjecture of this sort hazardous.

Thus, in spite of the care used to determine solid volumes for buoyancy correction, there remains doubt of its precision. Furthermore, a 2% error in solid volume can be shown to produce as much as a 60% error in the data reduction of helium adsorption.

The most likely cause of the excessive scatter of the data was transient contamination of the sample by such materials as stopcock grease, plasticizer from various balance components, and even impurities in the sample gas which may have entered through the trap from time to time. Interestingly, if appreciable contamination were present, it adsorbed and desorbed reversibly with pressure changes at a given temperature. The stopcock grease contamination was seen to be not reversible at any measurement temperature, but rather could be reversed only at very high temperatures. Thus, some impurity, such as hydrogen, may have occasionally passed through the carbon trap, either when the trap was not adequately cooled or when it was "loaded" or "dirty."

Comparisons With Other Work. This work is not the only attempt that has been made to determine helium adsorption. Maggs *et al.* (*6*), Homfrey (*4*), and Steele and Halsey (*8*) have reported results which agree generally with this work.

On the other hand, Flood (*3*) has estimated the ratio of $\rho_a/\rho = 1.1$ for helium and carbon at room temperature, where ρ_a is the density of helium in the pore space and ρ is the bulk phase gas density. If the adsorbed amount is presumed to be $(\rho_a - \rho)V_p$ where V_p is the volume of the pore space, and if an apparent nitrogen monolayer on charcoal just fills the pores, then the KH-1 adsorption at room temperature (at one atmosphere) ought to be about 0.1 standard cc. per gram. These results show about one-fifth this amount.

Data Presentation. No particular significance has been attached to the method of plotting the data. In view of the scatter, a refined plotting seemed inappropriate. Further, except in the case of KH-1, the shape of the curve could possibly be considered to be other than a straight line. However, the straight line represents the data about as well as or better than some of the more conventional types of plots common to adsorption work.

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