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The Low Temperature Adsorption of Nitrogen, Oxygen, Argon, Hydrogen, *n*-Butane and Carbon Dioxide on Porous Glass and on Partially Dehydrated Chabazite

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During the past seven years a number of papers have been published describing a new method for measuring the surface areas of finely divided and porous materials.[1-6] The work reported on in the present paper was undertaken with a view to investigating the possible limitations that may exist in applying the method to porous materials in those instances in which the pores approach molecular size.

The details of the method for measuring the surface areas by means of low temperature adsorption isotherms have been presented before and need not be repeated here. It will suffice to point out that if the physical adsorptions for a number of materials are plotted according to the equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_mC} + \frac{(C - 1)p}{C(p_0)} \qquad (1)$$

for a multilayer adsorption,[3] a straight line is obtained from which v_m, the volume of gas required to form a monolayer on the adsorbent, can be calculated. v is the adsorption of the gas at pressure p, p_0 is its liquefaction pressure, and C is a constant. It has been found that a plot of $p/v(p_0 - p)$ against p/p_0 is always linear up to a relative pressure of about 0.35 provided the adsorption isotherm is of the sigmoid shape such as illustrated by that part of the isotherm in Fig. 1 below 0.7 relative pressure.

Out of several hundred materials for which data have been obtained only charcoal,[2] up to the present time, has been found to give a flat Langmuir type physical adsorption isotherm rather than the S-shaped variety for gases such as nitrogen near their boiling points. It was suspected that since partially dehydrated chabazite contains many very small pores, it might likewise fail to yield an S-shaped adsorption isotherm and might not be susceptible to having its surface area measured by the low temperature adsorption method. Furthermore, porous glass might be in the same category if its pores have sufficiently small diameters.

The present work comprises the determination of low temperature adsorption isotherms on these two porous solids, using nitrogen, oxygen, hydrogen, argon, carbon dioxide, and butane as adsorbates.

Experimental

The apparatus used was a previously described[5,6] standard adsorption apparatus consisting of a measuring buret, an attached manometer, an adsorption bulb, a vacuum pump and a McLeod gage. The dead space calibrations were made with helium at the temperature of the adsorption run.

The porous glass[7] used as one of the adsorbents was furnished by the Corning Glass Co. In some of the measurements "uncrushed porous glass" (measuring 1 cm. square by 0.5 cm. in thickness) was used; in others, the

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(1) Emmett and Brunauer, THIS JOURNAL, 59, 1553 (1937).

(2) Brunauer and Emmett, *ibid.*, 59, 2682 (1937).

(3) Brunauer, Emmett and Teller, *ibid.*, 60, 309 (1938).

(4) Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.*, 13, 28 (1941).

(5) Emmett, *Advances in Colloid Sci.*, 1, 1-36 (1942).

(6) Emmett, *Am. Soc. for Testing Materials*, 41, 95 (1941).

(7) Hood and Norberg, U. S. Patent 2,106,744.

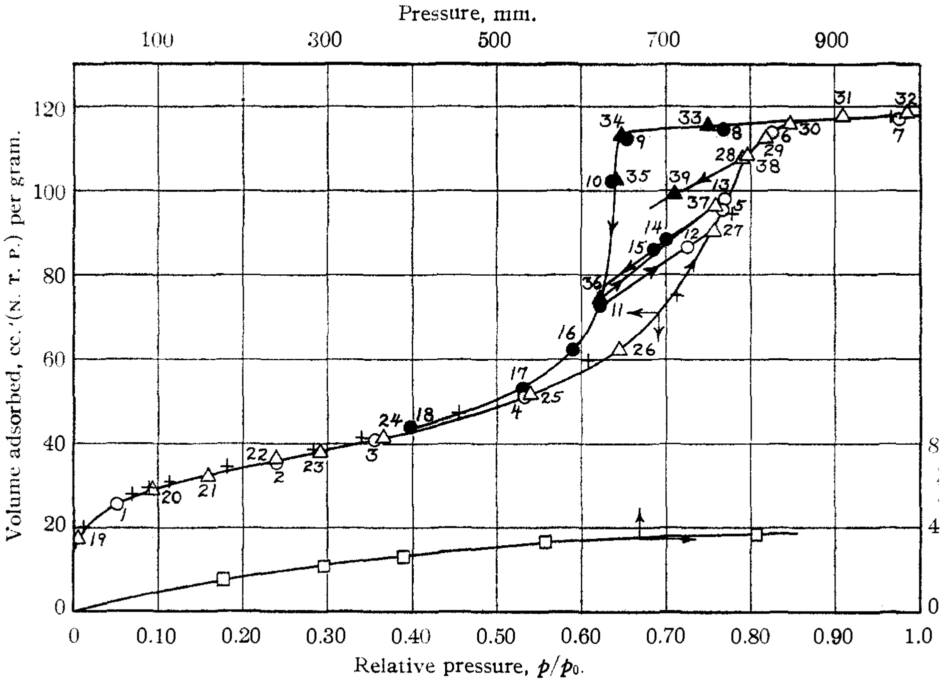

Fig. 1.—Adsorption of nitrogen on porous glass: ○, and △, runs 1 and 2, respectively, on crushed 48–80 mesh sample, 79.2°; +, uncrushed sample 3 × 10 × 10 mm. at 78°K.; □, crushed sample at 195°K. Solid points are for desorption. Numbers indicate order in which points were taken in runs 1 and 2.

glass was ground to between 48 and 80 mesh for the adsorption runs.

The chabazite was partially dehydrated by heating for fixed periods of time at successively higher temperatures. The loss of weight in the sample during evacuation at a particular temperature was measured by weighing the sample before and after the heating. The sample was dehydrated *in situ*, the adsorption bulb being attached to the adsorption apparatus by a ground joint. The cold baths were liquid nitrogen, liquid oxygen, acetone–dry-ice, and water–ice for −195, −183, −78 and 0°, respectively. The two lower temperatures were measured by an oxygen vapor pressure thermometer.

The gases used were taken from steel cylinders and purified as follows: oxygen and argon (99.5%) were merely dried; nitrogen and hydrogen were freed from oxygen by passage over hot copper and then dried; carbon dioxide was condensed in a liquid air trap and pumped free of inert gases.

Results

Porous Glass.—In Fig. 1 are shown the adsorption isotherms for two runs on nitrogen at about −194° on a crushed and screened sample of the porous glass, as well as for one run on an uncrushed sample, and also for a run at −78° on a crushed sample. It will be noted that the two isotherms on the crushed sample agree well with each other and also with the isotherm at −194° on the uncrushed glass. The equilibration time for each point at −194°, however, was about a day for the uncrushed compared to a few minutes for the crushed sample.

In two runs shown in Fig. 1, the upper part of the adsorption isotherm was studied in detail, an effort being made to throw some light on the nature of the hysteresis involved. Above a relative pressure of about 0.45, the hysteresis on the nitrogen curves was always in evidence. Below this pressure the adsorption and desorption curves superimpose. The hysteresis was further investigated by scanning. In some of the scanning, the desorption runs were interrupted at a relative pressure of about 0.625 and the pressure was increased; in others the pressure was decreased from some point on the adsorption curve until the desorption curve was reached. The course followed during the change from adsorption to desorption runs, or *vice versa*, is shown by the numbers which give the order in which the points were taken.

Figure 2 shows a curve for argon adsorption at −183° and one at −195°. The melting point of argon is about −189°. It is interesting to note that the shape and nature of the hysteresis is practically unaffected by the change from 6 degrees above the melting point to 6 degrees below, thus indicating that the condensed argon in the region of hysteresis is in the same state in both isotherms, presumably the liquid state.

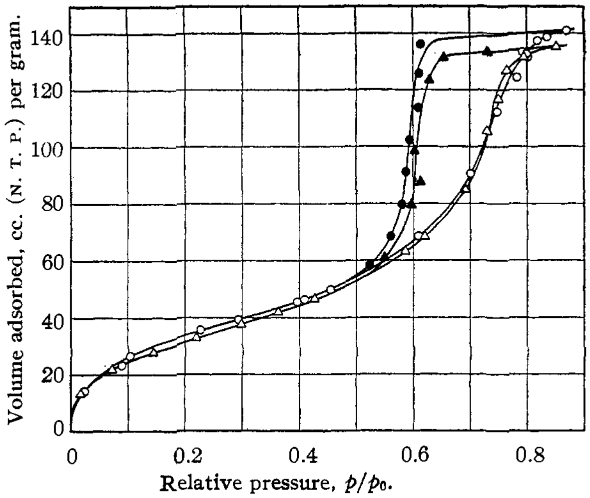

Fig. 2.—Adsorption of argon on crushed porous glass: ○, 79.3°K.; △, 90°K. Solid points are for desorption.

Oxygen isotherms on a crushed sample at −183 and −195° and on an uncrushed sample at −195° are illustrated by Fig. 3. Hysteresis effects are noticeable in these curves, though for some reason as yet unexplained the desorption curve failed to join the desorption curves but remained about 5% high. Whether or not this is a real effect is difficult to state until additional work has been done, though it was always obtained in the several oxygen runs made on porous glass.

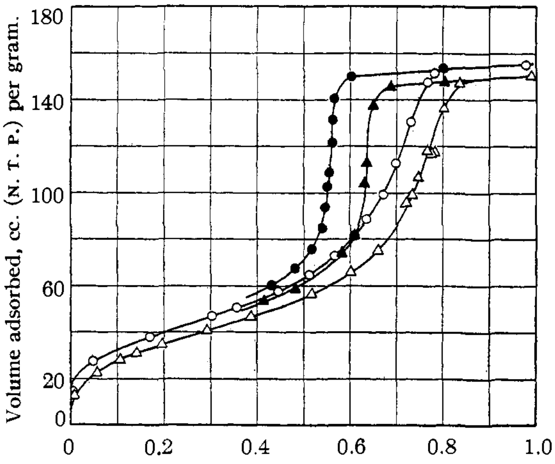

Fig. 3.—Adsorption of oxygen on crushed porous glass: ○, 78.3°K.; △, 90°K. Solid points are for desorption.

In Fig. 4 adsorption curves for butane and for carbon dioxide are shown. Desorption points were not obtained for butane nor for carbon dioxide. The carbon dioxide isotherm differs from the other isotherms in that it does not approach a maximum value as p approaches the vapor pressure of solid carbon dioxide. Apparently, the proximity to the pressure of liquefaction rather than to the pressure of solidification fixes the shape of the upper part of the isotherm and leads to the hysteresis observed for gases other than carbon dioxide.

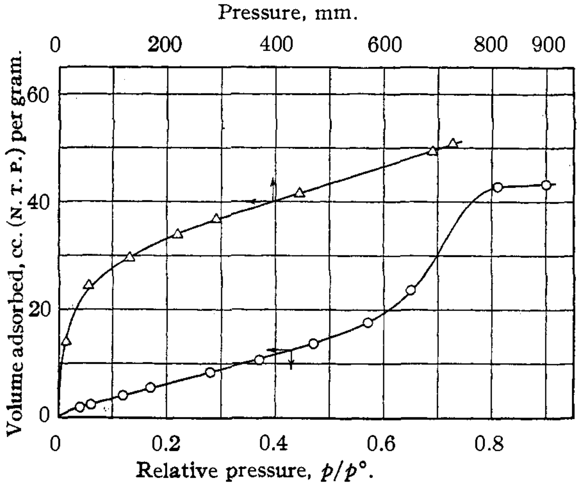

Fig. 4.—Adsorption of carbon dioxide and butane on uncrushed porous glass: ○, butane at 0°C.; △, carbon dioxide at 194.3°K.

Chabazite.—Figure 5 summarizes the results obtained in runs on a sample of chabazite that was about 50% dehydrated by seven hours evacuation at 120°. Perhaps the most striking result illustrated by the figure is the lack of detectable nitrogen adsorption at −195° on such a sample even though at the same temperature the hydrogen adsorption is about 15 cc. (N. T. P.) at a pressure of 200 mm. Furthermore, on this sample large adsorptions of carbon dioxide and of nitrogen can be made to take place at −78°. This is one of the few instances in which the amount of physically adsorbed nitrogen increases with an increase in temperature. Apparently, the pores resulting from 50% dehydration are too small to permit nitrogen molecules to enter at −195° at an appreciable rate even though they will permit the entrance of hydrogen at the same temperature. The enhanced adsorption of nitrogen at −78° is probably to be explained by the necessity of a considerable energy of activation in the process of diffusion into capillaries of molecular size that enables the adsorption to take place rapidly at −78° but not at a detectable rate at −195°.

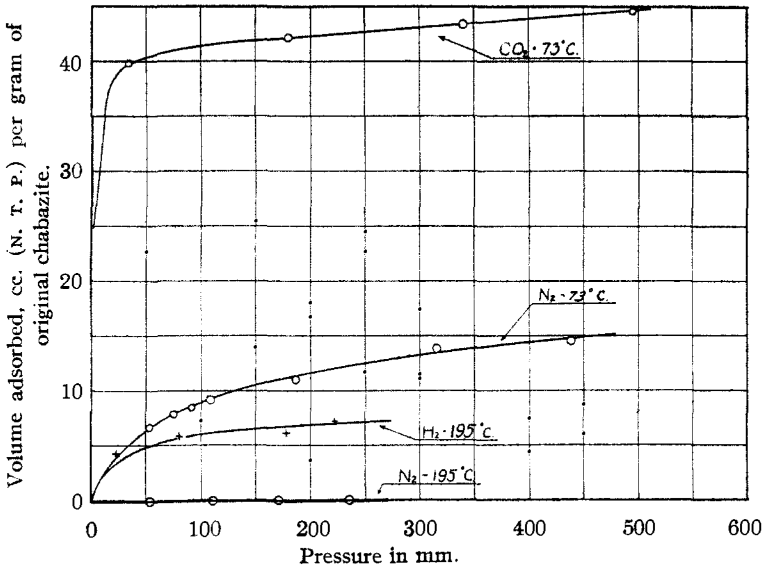

Fig. 5.—Adsorption of nitrogen, carbon dioxide, and hydrogen on crushed (100-mesh) chabazite dehydrated about 50%.

The curves shown in Fig. 5 do not correspond to true equilibrium. The three points on the carbon dioxide curve above 150 mm. pressure were still creeping, for example, at the rate of 1, 1.6 and 2.2 cc. per four hours, respectively, when taken.

Figure 6 illustrates the adsorption that takes place when 67% of the moisture of the chabazite was removed by evacuation up to 150°. Nitrogen adsorption at −195° is appreciable, amounting to about 12 cc. per gram of chabazite, though at −183° it is even larger than at −195°. However, the adsorption of nitrogen on this sample is considerably less than that of the smaller oxygen molecule. The latter attains a value of about 110 cc. at −194° and 100 cc. at −183°, and 200 mm. pressure. Argon is intermediate between oxygen and nitrogen. Considerable adsorption of oxygen and nitrogen at −78° occurs though the amounts are smaller in both cases than the corresponding adsorptions at −183°.

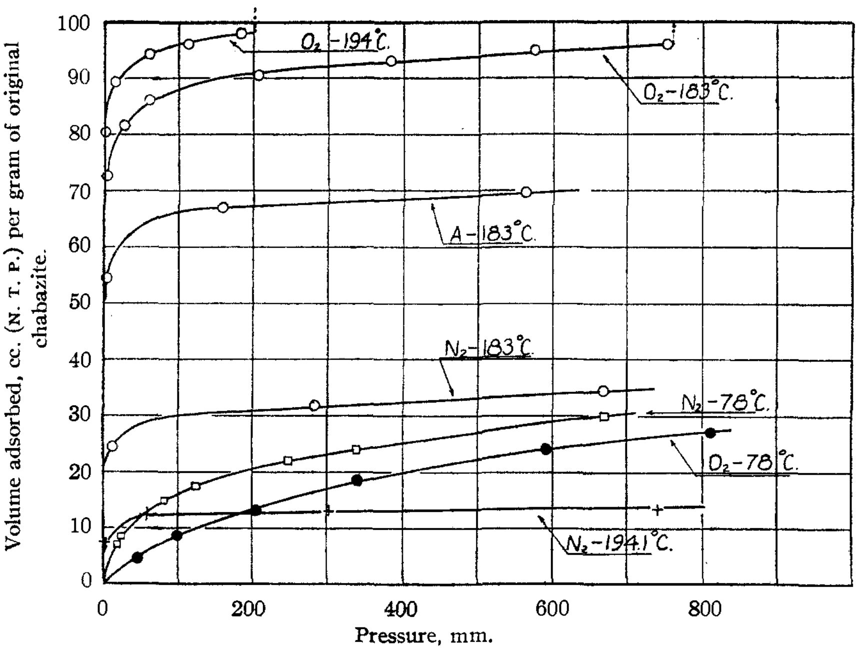

Fig. 6.—Adsorption of nitrogen, oxygen, and argon on crushed (100-mesh) chabazite dehydrated about 67%.

Curves in Fig. 6 like those in Fig. 5 are definitely not equilibrated. The oxygen adsorption at 60 mm. pressure, after three hours, was creeping 0.15 cc./hr. at −194° and 0.3 cc./hr. at −183°. Similarly the nitrogen adsorption at 60 mm. pressure after five and one-half hours was creeping 1.2 cc./hr. at −183° and 0.4 cc./hr. at −194°. The argon curve was changing at the rate of 8 cc./hr. at 60 mm. pressure at the end of forty minutes. Only the −78° curves in this figure seem to be equilibrated.

Dehydration of the chabazite at temperatures up to 480° *in vacuo* removed about 96% of the water, according to our measurements. The resulting adsorbent (Fig. 7) took up large quantities of oxygen, the adsorption being about 157 cc. of oxygen per gram at −195° and 150 cc. at −183°. The nitrogen adsorption increased enormously as a result of increasing the percentage dehydration from 67 to 96%, being about 138 cc. per gram at −194° and 136 cc. at −183°. The argon adsorption is a little smaller than either oxygen or nitrogen. Both nitrogen and oxygen adsorption at −78° increased several fold on raising the dehydration to 96%, though both of these adsorptions at −78° are only one-quarter to one-third of the value reached at −183°. The amount of butane taken up by the adsorbent is almost negligible, amounting to about 1 cc. per gram at a pressure of 200 mm. at 0°. Adsorption on the 96% dehydrated sample seemed to equilibrate fairly rapidly for all of the gases except argon, which equilibrated very slowly. Six hours time was required to get the first equilibration point on the argon isotherm. Accurate rate measurements were not taken on this sample.

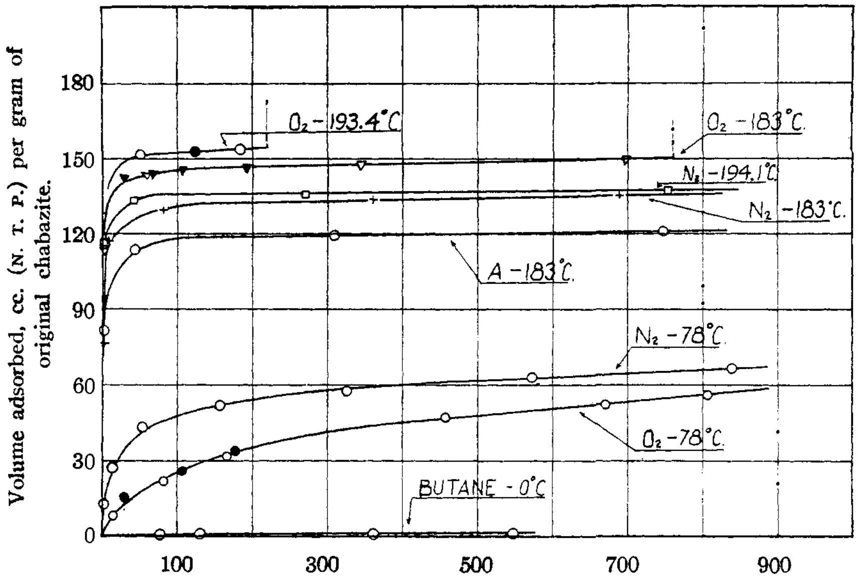

Fig. 7.—Adsorption of oxygen, nitrogen, argon and *n*-butane on crushed (100-mesh) chabazite dehydrated about 96%.

Discussion

Porous Glass.—By plotting the adsorption isotherms up to relative pressures of about 0.4 as $p/v(p_0 - p)$ against p/p_0 (Equation (1)) it is possible to obtain from the slope and intercept a value for v_m, the volume of adsorbed gas necessary to form a monolayer on the surface. This gives, in effect, the surface area of the walls of the tiny capillaries with which the porous glass abounds. From the saturation value of the adsorption as p approaches p_0 one is able to obtain a value for the volume of gas necessary to fill the capillaries on condensation to a liquid. By assuming that the density of the condensed liquid is the same as that of the normal liquid one can calculate the absolute volume of the space within the capillaries. In an obvious fashion, since the volume of the capillaries is $L\pi r^2$ whereas their surface is $2\pi Lr$, where r is the radius, and L the total length of such capillaries, the "average" radius of the capillary equals 2 times the volume to surface ratio. The values of r_v so obtained for oxygen, nitrogen, argon and butane are shown in column 3, Table I.

It is also possible to get an estimate of the pore size by applying the Kelvin equation

$$\ln p/p_0 = -2V\sigma \cos \theta/rRT \tag{2}$$

to the upper part of the adsorption isotherms for the above gases. σ is the surface tension, V the molal volume, and θ the angle of wetting. There

TABLE I

CALCULATIONS OF PORE SIZE AND PORE VOLUME OF POROUS GLASS FROM ADSORPTION ISOTHERMS

Gas	Temp., °C.	r_v Av. pore radius calcd. from volume:surface area ratio of pores	r_a Av. pore size by Kelvin eqn. Applied to steepest part of ads. isotherm	r_c Av. pore size by Cohan's eqn.[a]	r_d Av. pore radius from Kelvin eqn. applied to steepest part of desorption curve	$r_{max.}$ Radius of largest pores present in appreciable numbers, by Kelvin eqn.	Adsorption calcd. as volume of liquid per g.	Area of pore walls sq. m. per g.
Nitrogen	−195	30.2 Å	31–40	16–20	20.1	58	0.184	121
Argon	−195	32.0[b]	35–44[b]	18–22	25.1[b]	92[b]	.179	120
Argon	−183	31.4	29–35	15–18	19.7	57	.175	111.5
Oxygen	−195	31.8	33–46	17–23	22.8	63	.186	117
Oxygen	−183	31.6	33–45	17–23	22.8	61	.189	119.5
n-butane	0	50.8	29–48	15–24	..	61	.189	74.5

[a] r_c is equal to $r_a/2$. However, r_c is by definition[13] the radius of the cylindrical space in the capillary after a monolayer of gas is adsorbed on the walls. Supposedly, the radii of the empty capillaries would exceed the values shown in column 5 by one molecular diameter. [b] Extrapolated surface tension and density values of 14.9 and 1.42, respectively, for supercooled liquid argon at 79.1 °K. were used in these calculations. They are accordingly somewhat uncertain.

may well be a question as to the point on the curve at which the Kelvin equation should be applied. It has seemed likely that a suitable "average capillary" value could be obtained by making the Kelvin equation calculation at the value of p/p_0 at which the steepest part of the adsorption portion of the hysteresis loop occurred. The values for the radii, r_a, so calculated for the various gases are shown in column 4, Table I. The values for the surface tensions used in these calculations are 13.2 dynes/cm. for oxygen[8] at −183°; 16.1, for oxygen at −194°; 14.9, for argon at −194°[9a,b]; 11.9, for argon at −183°; 8.4, for nitrogen at −195°; and 14.94, for butane at 0°.[10] The corresponding density values for the liquefied gases are 1.14, 1.20, 1.42, 1.374, 0.799 and 0.60. The agreement between the capillary radii as given by r_a in column 4 and those calculated from the ratio of the pore volume to the pore surface as given in column 3 is fairly satisfactory for all the gases except butane. The Kelvin calculation for butane (column 4, Table I) agrees well with that for nitrogen, argon and oxygen; the r_v value obtained from the volume: surface ratio is about 40% higher as calculated from the butane curve than as calculated from the nitrogen, argon or oxygen isotherms. Perhaps this is not surprising, since there may be considerable uncertainty as to the actual cross-sectional area of the adsorbed butane molecule. If the area covered by the adsorption of a butane molecule is about 50% greater than the assigned value of 32 Å.,[2] the value of r_v in column 3, calculated from the butane isotherm would agree with those calculated from nitrogen, oxygen and argon.

The hysteresis noted in the upper part of the isotherms for oxygen, nitrogen and argon is a very reproducible and characteristic part of the curves. Each adsorption and desorption point on the porous glass isotherms was taken only after the pressure remained constant for at least one-half hour. Accordingly, both the adsorption and desorption curves correspond to an equilibration that changes only very slowly, if at all, with time.

The explanation of such hysteresis loops as shown in Figs. 1, 2 and 3 has been a matter of controversy for many years and cannot be stated with certainty even at the present time. Three theories for such hysteresis in systems having rigid cell walls have been put forth. They may be called the Zsigmondy theory[11] of partial wetting, the bottle-neck capillary theory of Kraemer[12] and McBain,[12a] and the open-end cylindrical capillary theory of Cohan.[13] These can be illustrated with the help of the curves in Fig. 1.

Zsigmondy believed that the angle of wetting might be much greater in adsorption than in desorption and that accordingly the equilibrium value of p/p_0 as calculated from equation 2 would be greater for adsorption than for desorption. To the extent that this change in the angle might be attributable to the presence of adsorbed gases and foreign matter on the surface of the adsorbent that would be displaced during adsorption, it must be ruled out in the present experiments on nitrogen and oxygen adsorption. Indeed, hysteresis of the kind illustrated by curve 1, Fig. 1, is so definitely established as a reproducible phenomenon even on carefully cleaned, highly evacuated samples that some explanation of it other than that offered by Zsigmondy will have to be found.

The bottle-neck theory of Kraemer and McBain postulates that the hysteresis may be due to the presence of capillaries with large bodies but narrow outlets. Condensation occurring in accordance with the Kelvin equation on a meniscus whose radius is that of the body of the capillary, r_b, would take place at a higher p/p_0 than evaporation from a meniscus whose radius is that of the capillary neck, r_n, where $r_n < r_b$. It is certainly possible that some of the hysteresis in Fig. 1 can be explained on this basis. However, when one remembers that the pores are formed by a leaching process, it does not seem likely that any preponderance of such pores with narrow necks and wide bodies would exist.

Cohan has suggested that hysteresis may be explained by the presence of capillaries having both ends open. Condensation in these would, he believes, occur on the walls of the capillaries according to the equation

$$\ln \frac{p}{p_0} = -\sigma \frac{V}{r_c RT} \qquad (3)$$

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[8] Baly and Donnan, *J. Chem. Soc.* (Transactions), **81**, 907 (1902).

[9] (a) The surface tension value and density for liquid argon at −194° had to be obtained by extrapolating since its melting point is −189°. The vapor pressure, p_0, used for argon at −194° is the value obtained by extrapolating from the data for argon above its melting point. (b) Landolt–Börnstein, "Tabellen."

[10] Coffin and Maass, THIS JOURNAL, **50**, 1427 (1928).

[11] Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911).

[12] Kraemer, "A Treatise on Physical Chemistry," edited by H. S. Taylor, D. Van Nostrand Co., New York, N. Y., 1931, Chap. XX, p. 1661.

[12a] McBain, THIS JOURNAL, **57**, 699 (1935).

[13] Cohan, *ibid.*, **60**, 433 (1938).

r_c being the radius of the cylindrical capillary opening after a monolayer of gas is adsorbed, and σ and V the surface tension and molal volume, respectively, of the adsorbate. On the other hand, Cohan postulates that desorption or evaporation from the capillaries after they are filled would occur at a meniscus according to equation (2). The following conclusions that would be drawn from such a theory may be compared with the experimental data: 1. The value of r at which hysteresis begins, r_h, should not be less than $2D$ where D is the diameter of the adsorbed molecules. In agreement with this r_h for the nitrogen isotherm is 9.8 Å. if one concludes from Fig. 1 that hysteresis begins at a value of 0.4 for p/p_0. Insufficient points were taken to fix with certainty the value of p/p_0 at which hysteresis began with argon, though it seems safe to conclude that r_h for the argon curves in Fig. 2 is not less than $2D$. In this connection it is interesting to note that adsorption data obtained by Higuti[13a] for a number of silica gel and titania gel samples show that r_h as calculated from equation (2) is approximately twice the molecular diameters of the adsorbed molecules.

2. The relation between the adsorption and desorption relative pressures for a given volume of gas adsorbed in the hysteresis region should, according to Cohan's paper, be given by the relation

$$p_d/p_0 = (p_a/p_0)^2 \qquad (4)$$

A glance at the hysteresis loops of Figs. 1, 2 and 3 will show that only when the comparison is made for P_a/P_0 values of about 0.8 or greater is good agreement with this relation obtained. For example, for P_a/P_0 values of 0.7 poor agreement with equation 4 exists, the calculated value for p_d/p_0 being 0.49 and the observed 0.56 to 0.62. Of course, if this equation were corrected for possible multilayer effects by using for equation (4) the extremities of suitable scanning curves, the agreement might be better. Such calculations must await more detailed scanning of the hysteresis loops.

3. The values of the radius of the average capillary calculated by equation (3) from the adsorption curves are shown in Table I, column 5. It is evident that the radii of the capillaries calculated in this way are somewhat smaller than the average values found by dividing the volume of the pores by the area of their surfaces, column 2. Similarly the values of the radii calculated from the Kelvin equation applied to the desorption data are (column 6, Table I) smaller than the average radii from the pore volume to pore area ratio.

Cohan points out that according to his open-end capillary theory no hysteresis should exist for capillaries in which any portion is as narrow as 4 molecular diameters, for closed end capillaries, for the space between parallel walls, or for wedge-shaped capillaries. It hardly appears likely that a sufficient number of cylindrical open-end capillaries would occur in any real adsorbent to account for the observed hysteresis.

The adsorption isotherms for porous glass are very similar to those to which Brunauer, Deming, Deming and Teller[14] recently applied an extension of the theory of multimolecular adsorption. In principle they attribute the leveling off of the upper part of such isotherms to the high heat of adsorption of the last layer of molecules taken up by narrow crevices. This theoretical treatment has, for simplicity, been limited to adsorption between two parallel walls and hence, strictly speaking, cannot be applied without modification to condensation in capillaries of other shapes. Nevertheless, the closeness of the fit obtained by them in applying their rather complicated equations to the data of Lambert and Clark[15] for the adsorption of benzene by iron oxide gel makes it probable that with sufficient effort approximate agreement can be obtained even in instances in which the capillaries can hardly be considered crevices with plane parallel walls. There certainly seems to be very good reason[3] for believing that the isotherms in Figs. 1, 2, 3 and 4 consist of multilayer adsorption at least up to the point at which hysteresis begins. No theory, up to the present, appears capable of explaining the hysteresis phenomenon without assumptions or postulates to which there is some objection.

Two additional characteristics of the isotherms should be noted. The radius calculation by equation (2) applied to the desorption curves will agree approximately with that from the volume to area ratio if one assumes that r is not the true capillary radius but the radius of the space left after covering the wall with the number of layers that one would statistically expect from the multilayer

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(13a) Higuti, *Bull. Phys. Chem. Research* (Tokyo), **19**, 951 (1940).

(14) Brunauer, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

(15) Lambert and Clark, *Proc. Roy. Soc.* (London), **A122**, 497 (1929).

adsorption theory. Thus if evaporation from the filled capillaries leaves two to three layers on the walls of the capillaries, the pore radius calculated from the nitrogen isotherms would be about 28 to 32 Å. Possibly a combination of this type of Kelvin calculation applied to the desorption curve and a statistical multilayer theory for the adsorption in capillaries will eventually lead to a satisfactory explanation of the observed hysteresis in adsorption isotherms.

Column 7 shows the apparent upper limit to capillary size as judged by the relative pressure above which practically no additional adsorption occurs. These upper limits as calculated by the Kelvin equation for the various isotherms in Figs. 1, 2, 3 and 4 give good agreement with each other in indicating that the largest pores are about 60 Å. in radius. Only the curve for the adsorption of argon at −195° seems to disagree. Since argon melts at −189°, it is entirely possible that its isotherm at −195° might not agree with those above its melting point.

In passing, one should also note that, as shown in Table I, the volumes of nitrogen, argon, butane or oxygen adsorbed by the porous glass at pressures approaching p_0 are substantially equal to each other. This is nearly true also of data previously reported for low temperature adsorption isotherms on charcoal,[2,16] though on charcoal there is a distinct tendency for the apparent pore volumes to decrease as the size of the molecule increases. The volumes of liquefied gas adsorbed at saturation agree much more closely as a matter of fact for porous glass as well as for charcoal than do surface areas calculated in the usual way from equation (1). For example, the volumes of liquefied gas required to fill the capillaries of porous glass range from 0.175 to 0.189 cc. per gram, as given in column 7, Table I. The maximum deviation from the mean is about 5%. The calculated surface areas, on the other hand, range from 75 to 121 sq. meters per gram, the maximum deviation from the mean being about 25%.

Little attention has been given to the question of the way in which gases are able to penetrate tiny capillaries such as are to be found in porous glass. Figure 1 shows that the isotherm made on an uncrushed sample of the glass measuring 1 × 1 × 0.5 cm. is substantially the same as for a 40–80 mesh sample. However, each point on the uncrushed sample required about twenty-four hours for equilibration compared to a few minutes for equilibration in the 40–80 mesh sample. It seems very probable that flow into such tiny capillaries entails surface diffusion of adsorbed gas.[17]

Chabazite.—The adsorption isotherms for the various gases on chabazite resemble those previously reported for charcoal in that they are all Langmuir type curves, concave to the pressure axis throughout. There are, however, some striking differences:

1. Chabazite acts as a sieve permitting small molecules to enter but screening out big molecules. Thus nitrogen was not adsorbed at −195° even though hydrogen was adsorbed at the same temperature (Fig. 5); nitrogen was slightly adsorbed on a sample of chabazite that had been 67% dehydrated whereas oxygen was strongly adsorbed; and finally, only 1 cc. of butane was adsorbed at a relative pressure approaching unity compared to 150 cc. of oxygen at a similar relative pressure.

This screening effect is not new, O. Schmidt[18] having pointed out such an action by chabazite a number of years ago. It was, however, the first indication that by controlled dehydration the capillaries could be made so small as to exclude even nitrogen molecules. Clearly the surface area of chabazite cannot be measured by low temperature isotherms.

In contrast to chabazite, charcoal has been shown to adsorb butane, nitrogen, argon and oxygen in quantities that at saturation represent approximately the same volume of liquid in each instance.[2,16]

2. The comparison of the volumes of liquefied gas adsorbed per gram at saturation shows 0.212, 0.188 and 0.157 cc. of nitrogen, oxygen and argon per gram of chabazite compared to 0.294, 0.284 and 0.268 cc. nitrogen, oxygen and argon, respectively on charcoal.[2] It appears, therefore, that for some reason argon is much less adsorbed on chabazite than one would expect.

3. Equilibration of the gas with chabazite is very slow, indicating that the gas has to enter the adsorbent by travelling through very small capillaries. In contrast to this, charcoal equilibrates rapidly, indicating probably somewhat larger pores than those in chabazite and also some larger feeder capillaries by which gas can quickly penetrate the individual particles.

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[16] Lamb and Coolidge, This Journal, **42**, 1166 (1920).

[17] Clausing, *Ann. Physik*, **7**, 489 (1930).

[18] Schmidt, *Z. physik. Chem.*, **133**, 280 (1928).

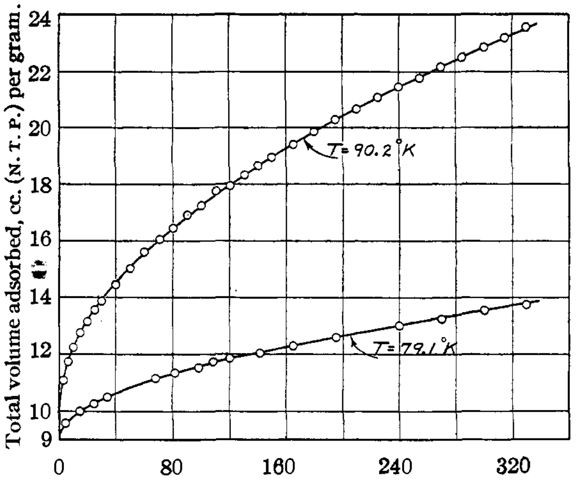

Fig. 8.—Rate of adsorption of nitrogen at 60 mm. pressure on chabazite 67% dehydrated.

Lamb and Woodhouse[19] have studied the adsorption of oxygen, carbon dioxide and hydrogen at 0° on samples of chabazite dehydrated to extents ranging from about 30 to 97%. They noted that increasing the percentage dehydration from 90 to 96% caused the oxygen adsorption to increase two-fold with no increase in the carbon dioxide adsorption. This result was interpreted as indicating the opening up of small capillaries during extended dehydration, these small capillaries being large enough to admit oxygen but not carbon dioxide molecules. The runs obtained in the present work indicate a very decided preferential increase in the adsorption of nitrogen molecules relative to the smaller oxygen molecules as the per cent. dehydration increased from about 50 to 90%. Actually, the nitrogen adsorption increased about 11-fold between 67% dehydration and 96% dehydration whereas that of oxygen increased only 60%. Nothing in the results of Lamb and Woodhouse would lead one to expect such a relative increase of nitrogen adsorption with respect to oxygen adsorption. However, the choice of gases, temperature, and percentage dehydration in their experiments and ours do not overlap sufficiently to warrant a very critical intercomparison of the two sets of results.

The isotherms that we obtained on the largely dehydrated chabazite are in good agreement with those obtained recently by Barrer[20] for nitrogen at −195°. However, he worked on only the completely dehydrated samples and therefore did not notice the gradual relative increases of the adsorption of the several gases with increase in the per cent. dehydration of the chabazite.

A few measurements on the rate of adsorption at a given pressure were made for nitrogen at −195 and −183°, on a sample of chabazite that had been 67% dehydrated by evacuating to 150° for seven hours. After an initial rapid rise the adsorption at a given pressure began to increase with the square root of the time. The rate curves are shown in Fig. 8; the plots of volume adsorbed against $\sqrt{\text{time}}$ are given in Fig. 9. Such linear dependence of volume adsorbed on the square root of time is usually construed as resulting from diffusion process obeying the Fick[21] diffusion equation. On the assumption that the temperature coefficient of the rate measurements indicates a certain energy of activation required to cause a nitrogen molecule to diffuse down a capillary of molecular dimensions, the temperature coefficients of the rates when 11, 12 and 13 cc., respectively, have been adsorbed correspond to 3830, 3650 and 3340 calories. These appear to be reasonable in magnitude.

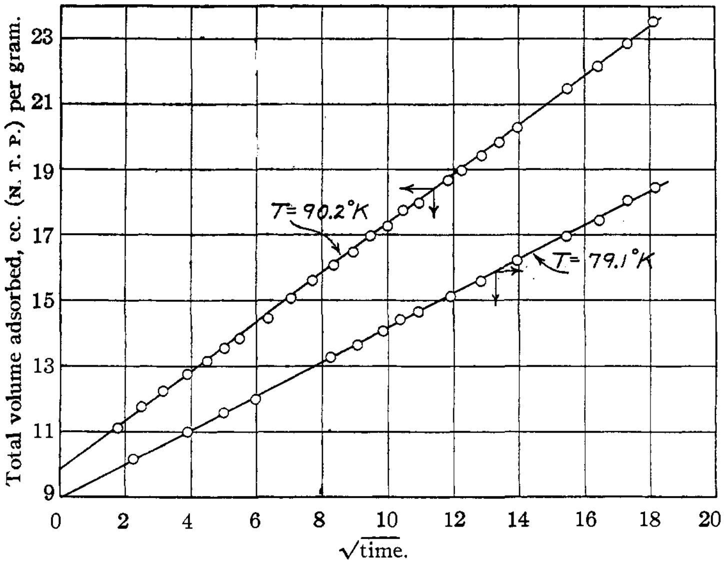

Fig. 9.—Rate of adsorption of nitrogen at 60 mm. pressure on chabazite 67% dehydrated.

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(19) Lamb and Woodhouse, THIS JOURNAL, **58**, 2637 (1936).

(20) Barrer, *Proc. Roy. Soc.* (London), **A167**, 393 (1938).

(21) Emmett and Brunauer, THIS JOURNAL, **56**, 35 (1934).

Summary

1. The adsorption of nitrogen, oxygen, hydrogen, argon, carbon dioxide and *n*-butane has been measured on porous glass and on partially dehydrated chabazite near the respective boiling points of the gases.

2. The surface area of porous glass can apparently be measured satisfactorily by the low temperature gas adsorption method; chabazite, on the other hand, when only 50% dehydrated adsorbs no nitrogen at −195° but will adsorb considerable hydrogen at −195° and carbon dioxide at −78°.

3. The occurrence of reproducible hysteresis loops in the adsorption–desorption curves on porous glass has been noted and discussed.

4. The average pore size of the porous glass has been calculated by various methods. The largest pores were about 60 Å. in radius as calculated by the Kelvin equation from the low temperature isotherms for argon, oxygen, nitrogen or butane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Molecular Surface Energy of Sulfur Dioxide Addition Compounds. II[1]

BY J. RUSSELL BRIGHT[2] AND JOSEPH J. JASPER

In a recent article[3] the effect of temperature on the molecular surface energy of the readily dissociated addition compound of sulfur dioxide with dimethylaniline, $C_6H_5(CH_3)_2N\cdot SO_2$, was presented. The purpose of this investigation was to extend the same physical measurements, over the temperature range 0 to 30°, to a more stable liquid addition compound of a tertiary amine with sulfur dioxide.

It was known[4] that gaseous sulfur dioxide reacts with triethylamine at room temperature to form a red, oily liquid, which by distillation under normal pressure gave a clear, light yellow to light green distillate; freezing point of product, −31.8°. Therefore, the triethylamine–sulfur dioxide complex was a logical one for study.[5] The density[6] and surface tension[7] of triethylamine at 20°, for example, are 0.7274 g./ml. and 20.9 dynes/cm., respectively; the Eötvös constant is 1.72.

Experimental

Preparation of the Liquid Molecular Addition Compound.—One mole of the best grade Eastman Kodak Company triethylamine, purified in the usual manner by distillation and drying over freshly cut sodium, was placed in a Florence flask. The index, $n^{20}\text{D}$ Abbe, of the sample was 1.4010. One mole of gaseous sulfur dioxide was purified and added as previously described.[3] During the reaction, noticeable heat was evolved and the product obtained had a deep red color. Distillation in an all-glass apparatus gave a nearly colorless product, b. p. 93.5° (751 mm.), f. p. −32°, $n^{20}\text{D}$ 1.4840. Freshly prepared material was analyzed for nitrogen by a modified Kjeldahl method: found N, 8.36%, 8.15%; calculated for $(C_2H_5)_3N\cdot SO_2$, N, 8.47%. The compound remains stable for an indefinite period as a white solid at the temperature of dry-ice. It is extremely hygroscopic and the liquid on exposure to moist air forms a voluminous white solid, which we have not yet investigated. Cryoscopic determination of the molecular weight, using purified benzene, f. p. 5.4°, gave 165.87, 164.65, 165.26; theoretical 165.19.

Procedure.—Since it was necessary to protect the compound from moisture, density measurements of the anhydrous substance were made in a manner somewhat different from that described in the first article of this series.[3] The 20-ml. pycnometer was fitted with a 10-cm. capillary tube of large bore (*ca.* 2.8 mm.) in which the liquid expanded as the temperature was raised. A stopcock and a standard ground-glass connector, sealed to the outer end, permitted evacuation of the pycnometer and facilitated transfer of the sample to it without exposure to the air. Increase in volume with temperature was readily followed and determined with the aid of a cathetometer. Water was used to calibrate the pycnometer. The precision of the temperature measurements was ±0.02°.

Surface tension measurements were made by the method already described,[3] using a capillary height apparatus with a capillary of 0.19168 mm. radius. The equation[8] sug-

$$\gamma = \frac{\left(h + \frac{r}{3}\right)(d_1 - d_a)gr}{2}$$

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Memphis meeting of the American Chemical Society, April, 1942.

[2] Present address: Gelatin Products Co., Detroit Mich.

[3] Bright and Jasper, THIS JOURNAL, **63**, 3486 (1941).

[4] Bright, Dissertation, The Ohio State University, June, 1940.

[5] It is recognized that Jander and Wickert, *Ber.*, **70**, 251 (1937), state that triethylamine dissolved in liquid sulfur dioxide forms a yellowish colored solution, which on evaporation of excess solvent gave a white, crystalline compound, melting point, 73°. These authors formulated this substance as $(Et_3NSO_2)_n$ or as a thionyl di-(triethylammonium)-sulfite, $[(Et_3N)_2S]SO_3$, and presented many chemical reactions to substantiate this peculiar formulation.

[6] Swift, THIS JOURNAL, **64**, 115 (1942).

[7] "Int. Crit. Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 435.

[8] N. E. Dorsey, "National Research Council Bull.," No. 69, p. 56.