

ence in binding energies for unoriented and oriented planes would be less than the difference in mean binding energy for the artificial graphite between 15° and 1118° C. of 0.40 kcal. per mole, and Planck's equations can be applied in the simple manner described.

As suggested by Brennan, graphite may be considered an idealized molecular crystal with each layer plane an independent molecule. Expansion studies by Nelson and Riley and the authors bear this out by showing insignificant interaction between the in-plane bonds in each molecule and the bonding between planes. That is, an appreciable change in the bonding distance between molecules showed, at best, a minute change in the in-plane bond distances. This is reasonable if one compares the strength of the in-plane bonds of approximately 40 kcal. per mole (meaning that each carbon atom in the plane is held with a combined energy amounting to 120 kcal. per mole) with the much lower bonding energy between molecules. Therefore, even though the interplanar bonding energy between the molecular graphite planes shows a substantial decrease of 13% in going from room temperature to 1118° C., such a decrease would not be expected to significantly affect the ease of pulling a carbon atom from a molecular plane (or the gasification rate), since this should chiefly be determined by in-plane bonding.

The x-ray examination of graphitized carbon during reaction with oxygen and carbon dioxide, within the limitations of the experimental technique, bears out the belief that the reacting gases do not penetrate the crystal lattice. It must be recognized, however, that the graphitized carbon is composed of an agglomerate of minute crystallites and that all faces of all these crystallites may not be oriented in such manner as to permit contact between reactant gas and planar crystallite edges. If, as might be possible, considerable orientation of crystallites occurs during graphitization, it is conceivable that penetration of the reactant might be prevented by unfavorable orientation rather than the present inability to do so under the conditions investigated. Certainly a more direct investigation of the possibility of oxygen penetration during reaction would be the use of a single graphite

crystal. Here the reacting gas would have access to all the interplanar spaces of the solid and the presence or absence of interplanar penetration could be more accurately determined and related to the reaction mechanism. The results obtained here, however, should be indicative of the reaction mechanism possible for artificial graphites and carbons of the type investigated.

ACKNOWLEDGMENT

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Adsorption-Desorption Studies of Nitrogen, Argon, and Carbon Dioxide on Carbon Rods

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LOW temperature gas adsorption is a convenient technique for obtaining information of the surface area and pore structure of solids. However, when the areas determined by this technique are related to the gasification or combustion properties of carbon at high temperature, a question arises as to whether or not the area available to a gas molecule at low temperatures is in any way comparable to the area available to the same molecule at elevated temperatures. The answer to this question would be expected to depend primarily upon the pore structure of the carbon under investigation, with carbons containing numerous pore constrictions likely to show the greatest effect of temperature on the availability of their area.

Recent work on the surface areas of coal and coal chars indicates that these solids act like molecular sieves. Maggs and

Bond (12), for example, find that the internal structure of bituminous coal chars can be pictured as a collection of large pores connected to the surface by molecular size capillaries. They find that over 55% of the area of some chars lies beyond pore constrictions 5.7 A. or less in diameter. Malherbe (13, 14) finds that B.E.T. surface areas determined for South African coals are a function of the adsorbate used. If room temperature adsorbates such as methanol or water are used, the surface areas are as much as 30 times higher than areas determined for low temperature argon adsorption. This difference is attributed to the swelling of the coal by the methanol or water with the resulting penetration of these molecules into previously unavailable molecular capillaries. Lecky, Hall, and Anderson (10) recently compared the adsorption of water and methanol vapors on American

The present investigation was undertaken to study the nature of low temperature sorption of gases on carbon rods used in previous gasification studies. From this study it was hoped to learn more about the pore structure of the carbon rods and to clarify the relation between "low temperature" and "high temperature" area. A gas-baked and a graphitized carbon rod, both previously reacted with carbon dioxide at 1300° C. to a weight loss approximating 10%, were studied. Sorption of nitrogen produces the usual Type II isotherm with a hysteresis loop above a relative pressure of 0.4. Argon adsorption on gas-baked carbon is similar to that of nitrogen; however, on graphite a hysteresis is present down to a relative pressure of 0.02. The sorption curves of carbon dioxide on both carbons show a hysteresis loop over the relative pressure range studied, 0.02 to 0.45. After putting an initial adsorption volume on the carbons, the samples were outgassed for different lengths of time and the re-adsorption volumes determined. The adsorption of argon and nitrogen at -196° and -192.5° C. is partly irreversible even for outgassing times up to 24 hours; however, the adsorption of carbon dioxide at -78° C. is completely reversible in less than 5 minutes outgassing time. The indication is that the initial adsorption of nitrogen and argon involves the partial penetration of these gases into molecular size capillaries, which are quickly closed off by other adsorbed molecules. These gases then penetrate deeply into the porous network and at low temperatures either lack sufficient energy to diffuse back to the surface or require a much longer time to do so.

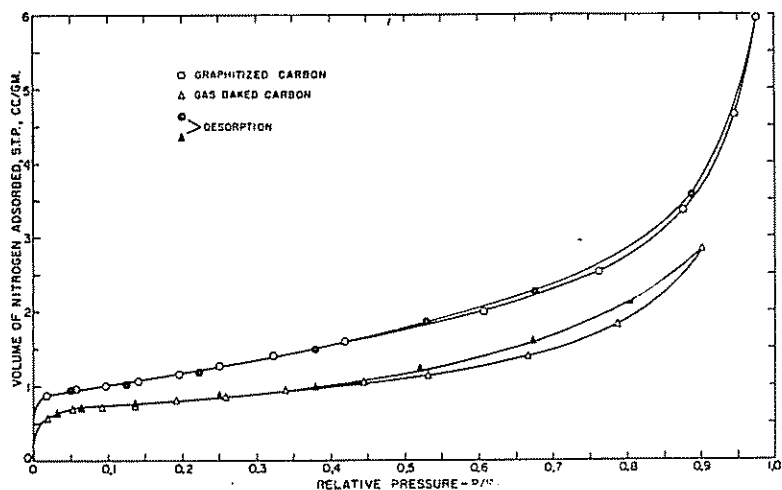


Figure 1. Sorption Isotherms of Nitrogen on Carbon Rods at 77° K.
One gram reacted at 1300° C.

coals with low temperature nitrogen adsorption and found that the vapor adsorption gives areas as much as 200-fold higher than low temperature nitrogen adsorption. Emmett (5) reports that the surface areas determined for finely divided graphite are a function of the size of the gas molecule, with the area determined by salicylic acid lower than the nitrogen area by a factor of 10. Walker, Foresti, and Wright (17) show that surface areas of gas-baked carbon and graphite, determined by the low temperature adsorption of carbon dioxide, nitrogen, and argon, are dependent on the size of the gas molecule, with the argon areas being about 15% higher than the carbon dioxide areas. These findings indicate that a considerable fraction of the area of many types of carbon are reached through small capillaries.

The present investigation was undertaken to study in more detail the nature of low temperature sorption of gases on carbon rods used in previous gasification studies. From this study it was hoped to learn more about the pore structure of the carbon rods and to

clarify better the relation between "low temperature" and "high temperature" area.

Gas-baked and graphitized carbon rods prepared from the same starting materials and subsequently reacted with carbon dioxide at 1300° C. to a weight loss approximating 10% were used in the investigation. A description of the method of preparation and analysis of the carbon samples and of the low temperature adsorption procedure are adequately covered in an accompanying paper (17).

RESULTS

Sorption Isotherms of Nitrogen, Argon, and Carbon Dioxide. Figure 1 presents the sorption isotherms of nitrogen at 77.1° K. on the graphitized and gas-baked carbon rods up to a relative pressure of about 0.9. The hysteresis loops closing at a relative pressure of about 0.4 are generally attributed to capillary

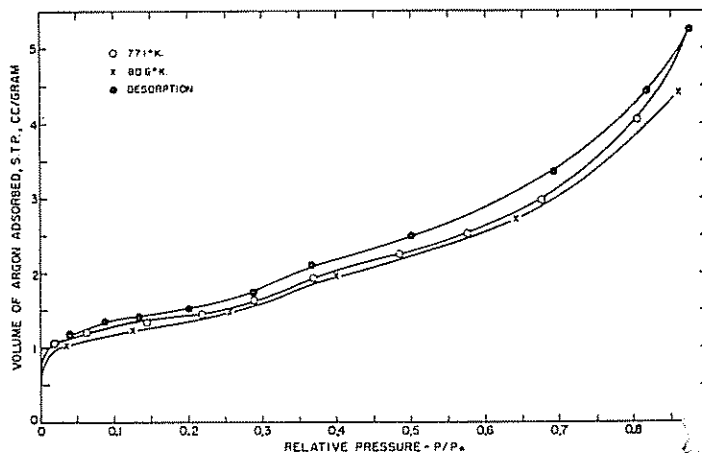


Figure 2. Sorption Isotherms of Argon on Graphitized Carbon Rods at 77° K.

One gram reacted at 1300° C.

condensation (2). The hysteresis loop for the gas-baked carbon sample is larger than that for graphitized carbon despite the fact that the volume of nitrogen adsorbed is twice as great in the

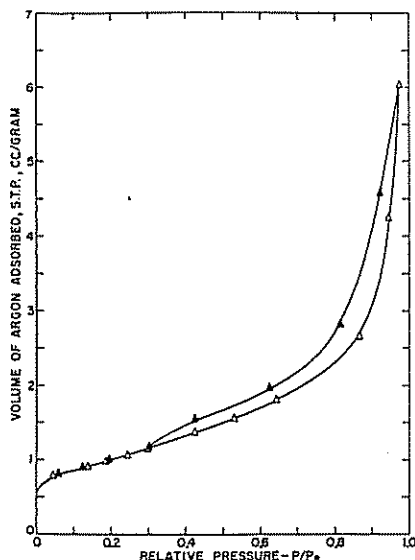


Figure 3. Sorption Isotherms of Argon on Gas-Baked Carbon Rods at 77° K.

One gram reacted at 1300° C.

Figures 2 and 3 present the sorption isotherms of argon on the graphitized and gas-baked carbon samples. The isotherms of argon on graphitized carbon present some seemingly significant variations from the nitrogen isotherms. At first thought, there would be every reason to believe that argon would give the normal closed hysteresis loop on this carbon—even more so than nitrogen. However, there is a definite hysteresis effect down to a relative pressure of at least 0.04. Normally such a hysteresis below relative pressures associated with capillary condensation are attributed to chemisorption. However, it is difficult to see how argon would be chemisorbed on graphite. Another interesting feature of argon adsorption on graphitized carbon is the kink or hump evident at a relative pressure starting around 0.3 on both the adsorption and desorption isotherms. Similar humps have also been observed by Malherbe (13) during desorption of argon on South African coals, by Corrin (3) during adsorption of argon on carbon blacks, by Gulbransen and Andrew (8) for adsorption of krypton on spectroscopic graphite, and by Polley, Schaeffer, and Smith (15) for adsorption of argon on heat-treated carbon blacks. Malherbe attributed the hump to a cluster of pores of a diameter corresponding to the value of relative pressure. This does not seem to be an entirely satisfactory explanation since no such hump is observed for nitrogen adsorption. In contrast to the adsorption of argon on the graphitized carbon, Figure 3 shows the normal hysteresis loop for adsorption of this gas on gas-baked carbon, with the loop closing at a relative pressure of 0.3. Although the adsorption curve shows no hump, the desorption curve breaks sharply at about 0.3.

The presence of a complete argon hysteresis loop on some carbons and not on others is again in line with the findings of Malherbe (13). He investigated the adsorption isotherms of argon on 15 different coals and found a well-marked hysteresis loop that

failed to close on 14 of the 15 samples. The one exception found the hysteresis loop closing at a relative pressure of 0.43.

Sorption isotherms for carbon dioxide on both carbons are presented in Figure 4. Because of the limitation of the apparatus, relative pressures higher than 0.45 were not possible for carbon dioxide. Both sets of isotherms show a marked hysteresis to as low a relative pressure as could be accurately measured. As neither adsorption isotherm shows the rapid rise due to capillary condensation, it would seem that the hysteresis could not be attributed to this cause. One would then suspect chemisorption in which case the carbon dioxide should be extremely difficult to remove from the carbon surfaces at low temperature. However, outgassing the samples at -78° C. for 5 minutes removed at least 96% of the carbon dioxide originally adsorbed at a relative pressure of 0.04. Indeed the hysteresis found for carbon dioxide adsorption seems to parallel that found for argon on graphite. Certainly for argon no chemisorption would be expected.

Effect of Low Temperature Outgassing Time on Subsequent Readsorption Volumes. To investigate further the nature of the adsorption-desorption process of gas on the carbon samples, studies were made of the effect of outgassing time on subsequent adsorption. In these experiments, an initial adsorption of gas was followed by outgassing for various lengths of time at both liquid nitrogen and liquid air temperatures and then by readsorption of the gas, always starting with the same initial gas pressure. Figure 5 shows the results obtained for both argon and nitrogen adsorption on the graphitized carbon samples. Approximately equal volumes were initially adsorbed in all cases. In no case did the time for obtaining adsorption equilibrium exceed 5 minutes. However, the adsorption process is irreversible with time. For example, at the end of 5 minutes initial adsorption is complete, but the maximum readsorption after 5 minutes outgassing time is less than 40% of the original volume adsorbed. It should be pointed out also that the readsorption equilibrium time was in all cases less than 5 minutes. Moreover, readsorption tests made after outgassing for 12 and 24 hours showed that the readsorption value remains below the original adsorption value even though the two readsorption values were virtually the same. These results can be attributed only to incomplete outgassing in the allotted time.

In order to determine the influence of temperature on the dependence of readsorption on outgassing time, studies were made at both 77.1° and 80.6° K. Figure 5 shows that this small change in temperature markedly affected the readsorption volume for outgassing periods up to several hours. For longer

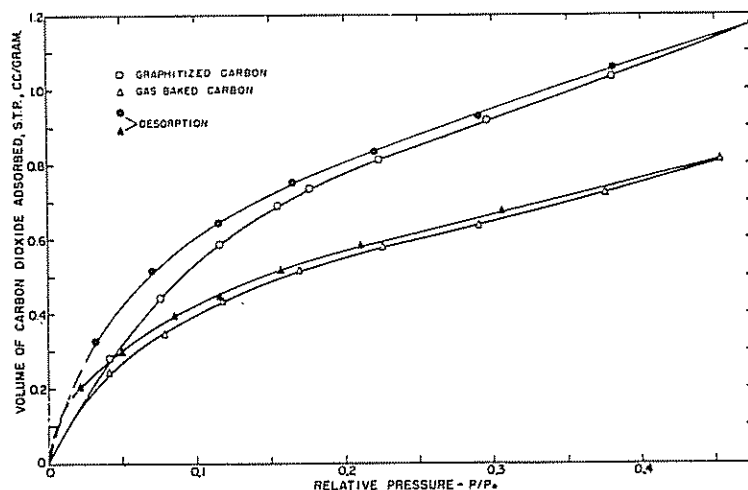


Figure 4. Sorption Isotherms of Carbon Dioxide on Carbon Rods at 195° K.

One gram reacted at 1300° C.

outgassing times, the effect is less pronounced suggesting the possibility of a continually decreasing steric factor.

Figure 6 shows the data of Figure 5 with comparable data for gas-baked carbon plotted as fractions of original volume readsorbed on the graphitized and gas-baked carbon samples. The readsorption volumes for the two carbons are virtually a constant percentage of the initial adsorption in all cases, although for the

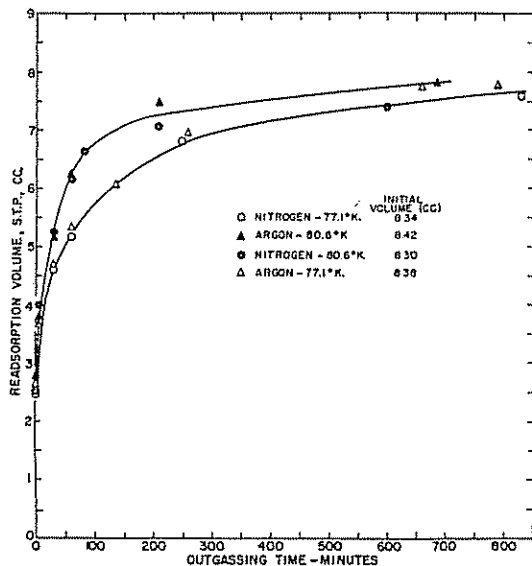


Figure 5. Gas Readsorption Volume vs. Outgassing Time after Initial Adsorption on Graphitized Carbon Rods

gas-baked carbon, because of its lower surface area, the amounts originally adsorbed are much less than for graphitized carbon. Similar data were obtained for carbon dioxide but are not reproduced as it was found that the ratio of readsorption volume to initial adsorption volume was essentially unity after only 5 minutes outgassing time at -78°C . for both carbons.

Relationship Between Readsorption Volume and Outgassing Volume. To determine the relationship between readsorption volume and the amount actually desorbed as a function of time, the initial adsorption volume of nitrogen and of argon on graphitized carbon was varied, the sample was outgassed for 30 seconds, and then the readsorption volume was determined. Following readsorption the sample was returned to room temperature, and the total amount of gas coming off the sample was determined. (Previous tests on adsorption of nitrogen and of argon and then returning the sample to room temperature showed excellent agreement between the amount adsorbed and the amount desorbed, which may be taken as an indication that for these gases all the sorbed gas is released from the sample at room temperature.) The difference between the total amount of gas that comes off at room temperature and the initial adsorption volume is then the net increase of gas that the sample picked up on readsorption. The difference between the total readsorption volume and this net volume increase is the actual amount desorbed in 30 seconds. Figures 7 and 8 show that the readsorption volume thus determined is greater than the desorption volume indicating an increase in total volume held on the sample with subsequent adsorptions. Both for nitrogen and argon the difference between the two volumes tends to decrease uniformly with decreasing initial adsorption volume down to the point of a monolayer volume. Below this point, the difference radically increases.

Furthermore, for both nitrogen and argon the desorption rate decreases linearly as the initial adsorption volume decreases; however, the desorption volume tends to zero while the initial

adsorption volume is still of an appreciable magnitude. For example, extrapolation of the nitrogen desorption curve in Figure 7 to the x-axis shows that when 5.8 cc. is initially adsorbed, none of this gas or at best a very small fraction is recoverable in the first 30 seconds of outgassing time. Then, as the volume increases beyond 5.8 cc., there is a fraction of the originally adsorbed gas that is recoverable in this time. It is further noted that as the initial adsorption volume increases the chief contribution to the difference between the initial adsorption volume and the desorption volume is that volume which is not removed in 30 seconds. For nitrogen, the differences in volumes are 5.8 and 7.0 cc. for 5.8 and 14.0 cc., respectively, initially adsorbed. For argon the differences in volumes are 8.0 and 10.0 cc. for 8.0 and 24.0 cc., respectively, initially adsorbed. That the volume difference should increase some with increasing initial adsorption is probably attributable to some increase in resistance due to blockage occurring in getting a larger volume of gas out of the macro-pore system.

Dependence of Readsorption Volume on Time. The data of Figure 5 for the effect of outgassing time on readsorption volume have been replotted in Figures 9 and 10, over a more limited

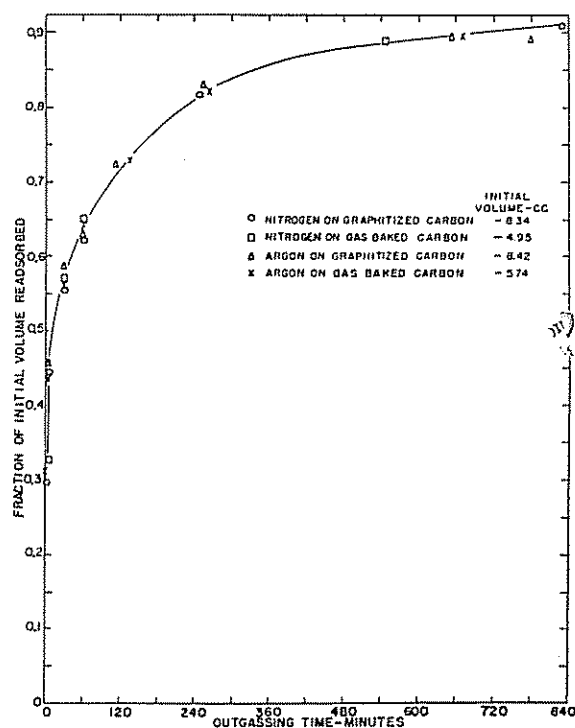


Figure 6. Fraction of Original Gas Volume Readsorbed after Different Outgassing Times at 77°K . for Graphitized and Gas-Baked Carbon Rods

time interval. The readsorption volume is here plotted versus the square root of time. Over the time interval from 5 to 60 minutes, the readsorption volume plots essentially as a straight line. Such a linear dependence of volume on the square root of time is normally construed as resulting from diffusion processes obeying the Fick diffusion equation. This correlation is not unexpected on the basis that readsorption volume is used, since Figures 7 and 8 show a definite relationship between readsorption and desorption volume. The decrease in readsorption volume for longer adsorption times should probably be interpreted meaning that the outgassing rate is no longer controlled by the diffusion of molecules through pore constrictions but by the decreased number of molecules striking a molecular outlet, where the diffusion would begin.

On the assumption that the temperature coefficient of the re-adsorption volume (or desorption rate) indicates a certain energy of activation required to cause a nitrogen or argon molecule to diffuse through the porous carbon, the temperature coefficient of the rate at different re-adsorption volumes can be calculated. For example, at a re-adsorption volume of 4.5 cc. of gas, the rate of increase of volume of argon re-adsorbed on the graphite rod with increasing time is 0.060 cc. per minute and 0.040 per minute at 80.6° and 77.1° K., respectively, giving an activation energy of 1.4 kcal. per mole. Likewise, for nitrogen at the same re-adsorption volume, the rate of increase is 0.065 cc. per minute and 0.028 cc. per minute at 80.6° and 77.1° K., respectively, giving an activation energy of 2.9 kcal. per mole.

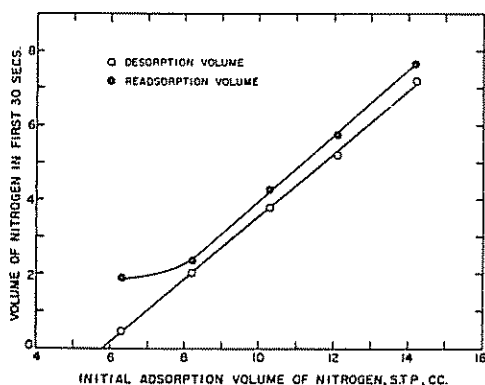


Figure 7. Irreversible Desorption of Nitrogen at 77° K. on Graphitized Carbon Rods

DISCUSSION OF RESULTS

The presence of a hump in the argon adsorption isotherm of graphitized carbon is in line with adsorption theories which have been pointed out by Smith and coworkers (15). That is, for monolayer adsorption the more homogeneous the surface the greater the attractive interaction forces between the molecules adsorbed. Consequently, at certain critical pressures (corresponding to the completion of monolayers) two-dimensional condensation begins, causing an inflection in the adsorption isotherm. The more heterogeneous the surface the less the molecular interaction in comparison to the interaction between the adsorbate and surface, and the humps are predicted to disappear. This is herein shown to be true for the more heterogeneous gas-baked carbon surface which did not produce a kink in the argon isotherm. It would further appear that an inflection in the adsorption isotherm is not only a function of the degree of heterogeneity of the surface but also of the adsorbate used. Nitrogen and carbon dioxide give no such humps even for graphitized carbon; this would seem to indicate that their surface interaction is sufficiently greater than that of argon to cancel the effect of molecular adsorbate interaction.

The work done on the desorption volume or rate versus initial adsorption volume is helpful toward an understanding of the low temperature adsorption process on the carbon samples. The results indicate that there is early entrapment of both nitrogen and argon molecules in the molecular pore structure. Apparently at the start of adsorption an appreciable volume of these gases is able to penetrate into the molecular structure. However, an adsorbed layer of gas is quickly built up around the molecular capillary entrances which blocks them from further gas penetration. On subsequent adsorption, only the carbon surface connected to the exterior of the sample by macromolecular capillaries is effective in adsorbing gas. This entrapment of gas molecules on porous carbon is not new. Dryden (4) reports that Maggs, on a sample of carbon in nitrogen, trapped the nitrogen in the pores, although this amount would not enter the pore structure if the sample were first cooled before adding the nitrogen. The trapped nitrogen was released on warming to -80° C. It is

difficult to explain why Maggs got no penetration of nitrogen into the molecular pore structure at liquid nitrogen temperatures, whereas the authors find that the gases readily penetrated at that temperature until blocking occurs. The possibility arises that the author's samples were not cooled completely to liquid nitrogen temperature upon the admission of the first adsorption volume but were quickly cooled to that temperature by the increased heat transmission produced by the gaseous atmosphere. However, this does not seem to be the case as the cooling time of several samples was varied from 1 to 4 hours, and no effect on the subsequent adsorption volume was noted. Moreover, a graphitized carbon rod exposed to an argon atmosphere as it cooled from room to liquid air temperature adsorbed only 7.70 cc., as compared to 7.48 cc. when the gas was admitted to the previously cooled sample. Even though the volume of gas adsorbed on the sample that was initially at room temperature is higher, this difference in volume is small compared to the amount of gas that was trapped on the graphite sample, as shown in Figure 8.

The fact that the diffusion into these pores is practically instantaneous compared to the outward diffusion can be explained in at least two ways:

1. There is no way of knowing how deeply a gas molecule does diffuse past the blocked off pore structure after measurable adsorption is completed. Therefore, the measured desorption rate of such molecules, due to their longer path of travel to the surface, would increase.
2. The average gas molecule diffusing in has a greater kinetic energy and hence a greater probability of getting through a pore opening than a gas molecule that must start from rest on the surface and diffuse outward.

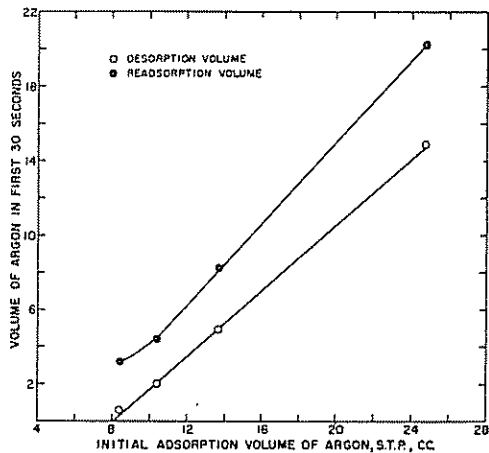


Figure 8. Irreversible Desorption of Argon at 77° K. on Graphitized Carbon Rods

It would seem that the complete hysteresis of the argon adsorption on the graphitized carbon sample could only be due to entrapment of some argon gas within molecular capillaries. However, even though outgassing tests show that nitrogen is also trapped in the gas-baked carbon samples at low temperatures, a nitrogen hysteresis was absent on these samples from a relative pressure of 0.4 to as low a pressure as was possible to accurately measure (0.02). The conclusion is that the trapped nitrogen consists entirely of gas placed on the surface during the initial adsorption. On the other hand, for argon on graphitized carbon apparently the initial blocking is not as complete (because of the smaller size of the argon molecule and its weaker force field), and some subsequent entrapment occurs. This subsequent entrapment would produce hysteresis and also a larger reported surface area for argon adsorption. The reason that argon does not produce a similar hysteresis for the gas-baked carbon is probably due

to its smaller average capillary diameter and, hence, complete blocking of argon at lower relative pressures.

It was suggested by Emmett (6) that the reason the desorption rate was much slower than the adsorption rate might be partially due to the greater heat of activation for desorption. It is interesting to calculate the approximate effect of increasing desorption energy on desorption time. Emmett (7) says that the desorption rate is determined principally by the frequency with

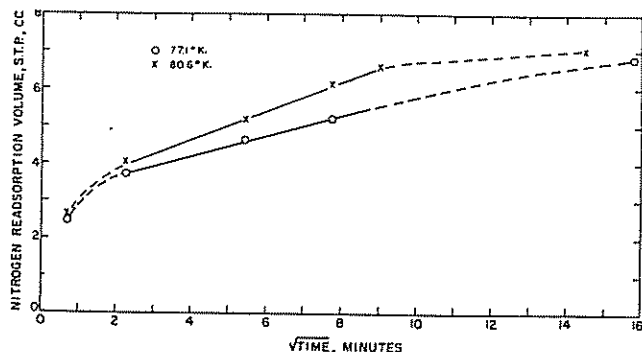


Figure 9. Nitrogen Readorption Volume vs. Outgassing Time after Initial Adsorption on Graphitized Carbon Rods

which a surface atom or molecule has an opportunity to readjust itself and gives, then, the rate of gas evolution by the following equation:

$$r = nfe^{-E_D/RT} \quad (1)$$

where

- r = rate of gas evolution in cc./sec./gram of sample
- n = number of cc. of gas constituting a monolayer on 1 gram of solid
- f = atomic vibrational frequency for the solid (commonly called the "restrahlen" vibrational frequency), 1/sec.
- E_D = energy of activation for desorption of the gas, kcal./mole

When n is always greater than a monolayer, the monolayer volume should be used, and when n is less than a monolayer, the average value of n over the desorption time should be used. For graphite, using the Debye characteristic temperature of 1946 (9) and the Debye specific heat curve (16), the atomic vibration frequency is 4×10^{13} . The energy of activation for desorption can be estimated from the equation

$$Q_{\text{adsorption}} = E_D - E_A$$

since E_A , the energy of activation for adsorption, should be negligible, as indicated by the very rapid adsorption speed at low temperatures. Hence, the energy of activation for desorption should essentially equal the heat of adsorption. Since the authors have no accurate data on the heat of adsorption of nitrogen in the monolayer on the carbon samples, the value of 3 kcal. per mole, determined calorimetrically on graphon by Beebe and coworkers (1), will be used. Graphon is a partially graphitized carbon black and should have a nitrogen heat of adsorption close to that of the graphite used in this investigation. For the graphite sample, the nitrogen monolayer volume is 0.95 cc. per gram so the time for outgassing this volume, if the energy of activation of desorption controls, is calculated to be $r = (0.48) (4 \times 10^{13}) e^{-3000/1.99 \times 77}$ or 5×10^4 cc./sec./gram. This, of course, is manifold greater than the desorption rate and, therefore, is not the controlling mechanism. The rate is very dependent on the value selected for the heat of adsorption. However, the selection of 3 kcal./mole is believed to be slightly

high, since it has been approximated by the B.E.T. equation that the adsorption heat of nitrogen on graphite is 2.1 kcal. per mole.

It is apparent that the existence of molecular capillaries in carbon can place a serious limitation on the interpretation of the relationship between area available for reaction and the area determined by low temperature gas adsorption. Physical adsorption of the gas molecules on the capillary walls at low temperatures is very effective in blocking off small pore entrances; whereas, at higher temperatures the gas molecules are chemisorbed on only the active site area, which, according to Long and Sykes (11), constitutes less than 2% of the total area. Hence, blockage of pore entrances would be much less complete. Furthermore, the fraction of gas molecules possessing sufficient energy to diffuse through such capillaries, if given by the usual Arrhenius coefficient, $e^{-E/RT}$, would be considerably less at liquid nitrogen temperatures. On the other hand, the fact that nitrogen and argon adsorption at -196°C . gives a greater surface area than carbon dioxide adsorption at -78°C . (17) does indicate that the size of the gas molecule also has a strong effect on the area available to it.

The present results would lead to the conclusion that the area available to an inert molecule at high temperature should be greater than the area available to the same inert molecule at low temperature for "bottleneck" carbons. However, in using low temperature adsorption to describe a high temperature area it must be kept in mind that the gas molecule at high temperature is not an inert. As discussed elsewhere (17), surface area studies,

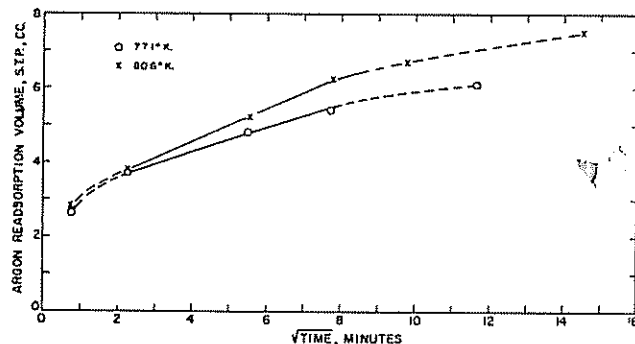


Figure 10. Argon Readorption Volume vs. Outgassing Time after Initial Adsorption on Graphitized Rods

where the low temperature area rapidly increases at the start of the gasification reaction and then becomes essentially constant, show that a reacting gas only uses that portion of the total carbon surface that is necessary to maintain the reaction rate at a given temperature. Therefore, a reacting gas at elevated temperatures is itself, in effect, utilizing only a fraction of the total surface area of the sample for reaction at any one instant. The question then is properly asked: What high temperature area is desired in correlating reaction rate results—the total area or the effective reacting area? It is apparent that low temperature adsorption on carbon rods of this type would not be expected to determine the total high temperature area available to an inert molecule. On the other hand, marked similarity between the change of reaction rate for the carbon-carbon dioxide reaction and the related low temperature surface areas (17) does indicate a possible strong connection between low temperature area and effective high temperature reacting area. This is probably due to the fact that pore constrictions are removed during reaction in the reacted area and, hence, appear as increase in low temperature area, whereas the total unreacted area still retains its pore constrictions. Therefore, low temperature adsorption does appear to be a useful and meaning tool to be used for the understanding of the gasification of carbon, but the limitations of the method for clarifying the high temperature mechanisms must be realized.

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