tions when the hydroxyl hydrogen is between its oxygen and a chlorine on the line of the carbon-chlorine bond.

Crude experiments show that the excess heat content of mixing of carbon tetrachloride–ethanol systems also passes through a maximum and a minimum.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

On the Adsorption of Gases by Graphite

BY ARTHUR B. LAMB AND EDWIN N. OHL

Careful measurements by Magnus and Kratz[1] have shown that both natural and artificial graphite adsorb carbon dioxide in modest amounts at 0°. This observation runs counter to current views as to the adsorptive properties of graphite, and indeed is somewhat surprising in view of the nearly complete saturation of the carbon atoms within the individual basal planes of the graphite crystal as evidenced on the one hand by their extreme involatility and on the other by the very weak cohesion between adjacent basal planes. Moreover, there is no evidence that the samples of graphite used by Magnus and Kratz were unusually finely ground or had any very considerable exterior surface.

A possible explanation of this unexpected behavior would be that the adsorption of the carbon dioxide takes place not only on the exterior surface of the graphite but also *within* the channels separating the basal layers of the carbon atoms in the crystal lattice. In this way a relatively huge inner surface would become available for adsorption, supplementing the relatively small outer surface of the powdered graphite.

Is such an invasion of gaseous molecules into the crystal lattice of graphite geometrically possible? On the basis of the recognized crystal structure of graphite the distance between the center of an atom in one basal plane and that of the nearest atom in the next adjacent plane is 3.40 Å. The distance between two carbon atoms linked together within the same molecule of aliphatic carbon compounds is about 1.5 Å. The difference, 1.9 Å., would represent the width of a channel in which repulsive forces would be relatively small and into which gaseous molecules, if they were small enough, might conceivably squeeze.

The smallest limiting diameter of the linear carbon dioxide molecule is certainly that of its oxygen atoms measured perpendicularly to the axis of the molecule. This is presumably not greatly different from the corresponding diameter of an oxygen atom in an oxygen molecule, and this in turn may be guessed as two thirds of the mean diameter of the molecule. This latter value, computed from the viscosity, is 2.9 and from the molecular refraction, 2.4 Å.; which would give 1.9 or 1.6 Å., respectively, as the smallest diameter of the oxygen molecule and hence also of the carbon dioxide molecule.[2] On this basis, these molecules might, therefore, conceivably make their way into the basal channels. With hydrogen the situation is more favorable; its mean diameter by the same methods of measurement is 2.3 and 2.0 Å., which would correspond to a smallest diameter of about 1.5 or 1.3 Å. If carbon dioxide could in any way invade the basal channels, hydrogen should do so much more freely.

Against the likelihood of any invasion of the basal planes, even if the molecules were small enough, is the consideration that the very forces of repulsion around the carbon atoms which prevent the closer approach of the basal planes to each other would prevent the ingress of other atoms. In rebuttal to this is the fact mentioned at the outset that the cohesive force between the basal planes is very weak, from which it follows that the repulsive force which balances it must be correspondingly weak. A further unfavorable consideration is the fact that the distance between the basal planes of graphite (3.40 Å.) is also the distance between contiguous carbon atoms of separate molecules of crystalline organic substances.[3] There is no evidence, so far as we are aware, that such substances display any adsorptive capacity for gases with small molecules, but it may be that this has never been adequately tested.

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[1] A. Magnus and H. Kratz, *Z. anorg. Chem.*, **184**, 241 (1929).

[2] Landolt–Börnstein, "Tabellen," 3rd Supplement, 1935, p. 105.

[3] W. L. Bragg, "Atomic Structure of Minerals," Cornell Univ. Press., Ithaca, N. Y., 1937, p. 54.

In support of the possibility of any such invasion is the fact that oxygen derived from powerful oxidizing agents such as chloric and nitric acid enters these basal channels to form laminated graphitic acid or oxide, although the measurements of Hoffmann, Frenzel and Csalán[4] show that the basal planes are thereby pushed apart so that the interplanar distance becomes 6 Å. or more. Hydrogen can also enter the basal channels, for Bangham and Stafford[5] have found that granular graphite exposed to an electric discharge in hydrogen gas at low pressure takes up hydrogen and thereafter is able to adsorb a not inconsiderable volume of oxygen gas. In rebuttal to this it may be urged that in both these cases the ordinary gaseous molecules may not be involved but rather free atoms or gaseous ions of the element.

To test this possibility more fully we have repeated the adsorption measurements of Magnus and Kratz with carbon dioxide on Acheson graphite and in addition have made similar measurements with hydrogen and difluorodichloromethane on the same material.

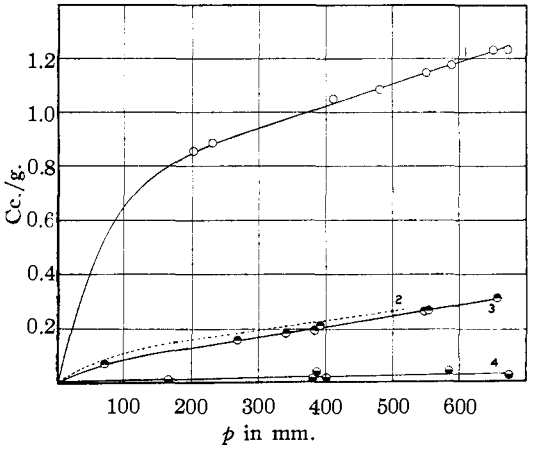

Fig. 1.—Acheson graphite at 0.0°: 1, CCl_2F_2 ○; 2, Magnus and Kratz ---; 3, CO_2 ◓; 4, H_2 ◒.

The graphite was commercial Acheson graphite of approximately 200-mesh fineness. Two combustions in a platinum crucible using oxygen gave a carbon content of 96.19 ± 0.04%, the residue being oxide of iron. Three measurements of density using toluene gave an average value of 2.269 ± 0.007.

The gases were commercial samples in cylinders; the carbon dioxide and difluorodichloromethane were purified by passing over calcium chloride and phosphorus pentoxide; the hydrogen by passing through outgassed, activated coconut charcoal, calcium chloride, potassium hydroxide and phosphorus pentoxide.

The apparatus was similar to that used by Lamb and Woodhouse.[6] In carrying out a measurement the adsorbent in the cell was maintained at 400°, and the system evacuated until the pressure as observed on the McLeod gage was 0.07 mm. or less. The reservoir was then charged with gas and after the adsorbent had been brought to the desired temperature successive portions of gas were introduced and the pressure read. The volume of the dead space was calculated from the measured volumes of the apparatus, allowance being made for the volume of the adsorbent as calculated from its density and weight. The uncertainty in this volume was, however, the limiting factor controlling the accuracy of our results, as the pressure, temperature and weight could all be measured with a greater relative exactness. The average uncertainty in the volume of adsorbed gas was about ±0.03 cc. The adsorption appeared to be complete within a few minutes and no change was observed when in some cases the gas was left in contact with the adsorbent overnight.

Our results, as well as those of Magnus and Kratz with carbon dioxide, are shown graphically in Fig. 1. It can be seen from this figure that our results for carbon dioxide are in reasonable agreement with those of Magnus and Kratz, particularly in view of the greater purity of their graphite. This agreement makes it quite certain that carbon dioxide is adsorbed by graphite in significant amounts at 0°. On the other hand, our results for hydrogen show that it is only very slightly adsorbed by graphite at this temperature, approximately only one-tenth as much as carbon dioxide, so that the relative adsorption of these two gases on graphite is not very different from their relative adsorption on activated charcoal. The inference is that no extra adsorption of hydrogen takes place in the basal channels of graphite and *a fortiori* that no such adsorption of carbon dioxide takes place. This conclusion is supported by our results with difluorodichloromethane, also shown in Fig. 1. This substance, of which the smallest molecular diameter is far too great to permit any invasion of the basal channels, is adsorbed much more extensively than is carbon dioxide.

A further possibility presents itself in the case of the carbon produced by the "explosion" of graphitic oxide. Since the distance between the basal planes in the oxide is 6 Å. or more, it appeared possible that the basal planes in the resultant carbon might retain to some extent this more open structure and thus provide a porosity

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[4] U. Hoffmann, A. Frenzel and E. Csalán, *Ann.*, **510**, 1 (1934), and U. Hoffmann and E. König, *Z. anorg. Chem.*, **234**, 311 (1937).

[5] D. H. Bangham and J. Stafford, *J. Chem. Soc.*, **127**, 1085 (1925).

[6] Lamb and Woodhouse, THIS JOURNAL, **58**, 2637 (1936).

into which the smaller but not the larger molecules could penetrate. Lowry and Morgan[7] have indeed found that carbon produced in this way does have a considerable adsorptive capacity toward carbon dioxide at 0° and nitrogen at −195°; some of their samples adsorbing one-fifth as much as activated coconut charcoal.

We have repeated the measurements with carbon dioxide and in addition have measured the adsorption of hydrogen, helium and carbon disulfide upon the material at this temperature.

Three samples of graphitic oxide were prepared following the general procedure of Staudenmaier,[8] starting with very finely divided Acheson graphite, No. 575 of the Acheson Colloids Corporation. The carbon disulfide was a pure commercial sample which had been shaken with mercury. The purification of the gases and the apparatus and procedure were the same as described above.

The results are presented graphically in Fig. 2 where the results of Lowry and Morgan with carbon dioxide are also included.

Our sample No. 3 shows about the same adsorption of carbon dioxide as was recorded by Lowry and Morgan; our sample No. 1 (curve 2) which was submitted to a particularly prolonged oxidation is decidedly more active, showing an adsorptive capacity about one-third that of very active coconut charcoal under corresponding conditions. The adsorption of hydrogen was very slight and that of helium inappreciable in spite of the relative smallness of their molecules. This shows that there is no inner surface accessible to the smaller but not to the larger molecules. Our results with carbon disulfide point the same way; although the smallest diameter of its molecule is certainly considerably larger than that of carbon dioxide, it is adsorbed, at corresponding pressures, ten times as extensively.

The considerable adsorptive capacity of this carbon shows, however, that during oxidation and subsequent explosion the graphite has either been changed decidedly in its atomic structure or its exterior surface has been greatly increased. An X-ray powder photograph of this material kindly made for us by Dr. S. Berman shows that the crystal structure of graphite is retained, but that the average diameter of the particles is about 30 Å. based on measurements of intensities. Assuming uniform cubical particles, this would afford a total surface of about 1000 sq. meters. This area is so much greater than that of the original graphite that it can fully account for the greater adsorptive capacity observed. Its area is of the same order as that estimated for active charcoal by many investigators.[9] Lowry and Morgan's view that the high adsorptive capacity of this material is due to "unsaturated carbon atoms" may of course be valid in whole or in part, but it is not necessary to make any such assumption to explain the observations.

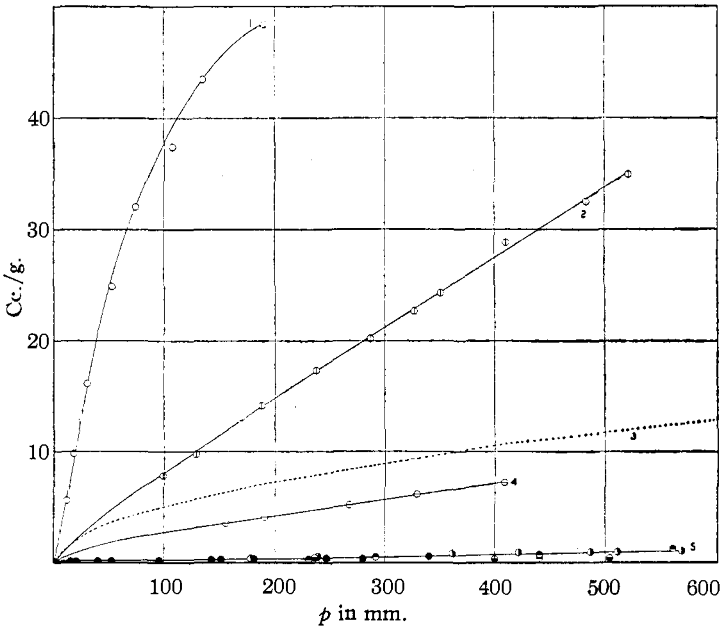

Fig. 2.—Carbon from graphitic oxides at 0.0°: 1, CS_2 on sample 3 ○; 2, CO_2 on sample 1 ⦶; 3, CO_2 Lowry and Morgan ---; 4, CO_2 on sample 3 ⊖; 5, Air on sample 1 ●; Air on sample 2 ◑; Air on sample 3 ◓; O_2 on sample 2 ◒.

A final possibility of obtaining graphite having a large surface accessible to gases through pores or channels of atomic dimensions and which might consequently exhibit a selective adsorption for smaller molecules was presented by the pseudomorphs sometimes obtained in the commercial manufacture and use of carborundum from which the silicon has been evaporated. These struc-

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[7] H. H. Lowry and S. O. Morgan, *J. Phys. Chem.*, **29**, 1105 (1925).

[8] L. Staudenmaier, *Ber.*, **31**, 1481 (1898).

[9] *Cf.* for example, J. W. McBain, "Sorption of Gases and Vapors by Solids," G. Routledge and Sons, London, 1932, p. 13.

tures retain the exterior crystalline form but not the surface luster of the carborundum. The crystal lattice of carborundum resembles that of the diamond, alternate carbon atoms being replaced by silicon atoms. The diameter of the silicon atom in this lattice appears to be practically that of silicon in its crystals, or 2.34 Å. When the silicon atoms escape there should be holes or channels of this diameter if no collapse of the crystal structure occurs and this space should be adequate for the entry of the smaller gaseous molecules.

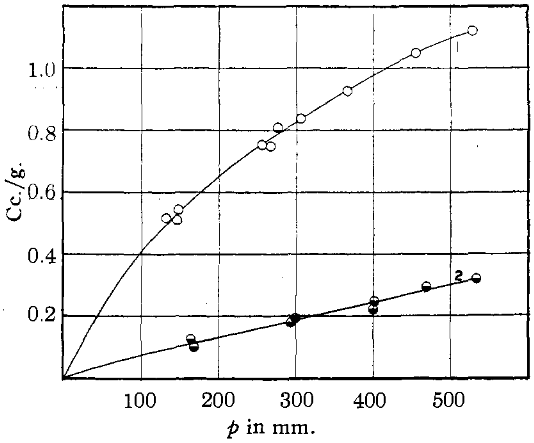

Fig. 3.—Adsorption of H_2 at −195.2° on: 1, Acheson graphite ○; 2, Carbon from SiC ◒.

A pseudomorph of this sort was kindly furnished us by Mr. H. D. Bachelor of the National Carbon Company. Two samples of it burned in a platinum crucible with the aid of oxygen indicated a carbon content of 99.92 ± 0.04%. Three measurements of its density with toluene gave 2.269 ± 0.007. We have measured the adsorption of hydrogen on this material at 0° and at −195.2°, as well as that of carbon dioxide and difluorodichloromethane at 0°. The adsorptions at 0°, even of the difluorodichloromethane, were so slight as to be no greater than our errors of observation. The adsorption at −195.2° was measurable and our results are shown in Fig. 3, together with similar measurements obtained at this temperature with the ordinary Acheson graphite used in our previous measurements.

It can be seen that the adsorption of hydrogen on this material at this temperature is exceedingly small, only about one-fourth of that observed on ordinary graphite. There is, consequently, not the least indication that the decomposition of the carborundum gives rise to any inner surface accessible solely or chiefly to the small hydrogen molecules. An X-ray powder photograph by Dr. Berman confirmed this conclusion. No definite trace of the carborundum pattern was discernible, while the lines characteristic of graphite were strong and sharply defined. Evidently the crystal lattice of the carborundum disappears under the extreme conditions of the distillation and the similarity of the structures to carborundum crystals is merely superficial.

The lessened adsorption of gases on this material as compared with ordinary Acheson graphite presumably is due to the greater perfection and size of the individual graphite crystals obtained at the high temperatures of the distillation and their consequent lesser external surface.

Summary

The observed adsorption of gases on graphite is not due to the entrance of the gaseous molecules into the spaces between the basal planes of the graphite crystal, but rather to adsorption upon the external surfaces of the crystallites.

The same is true as regards the much greater adsorption of gases upon the carbon produced in the "explosion" of graphitic oxide, although samples of this carbon were prepared which adsorbed nearly half as much carbon dioxide as does highly activated coconut charcoal.

Graphite obtained by heating silicon carbide until the silicon is gone, yet retaining the external form of the carbide crystals, adsorbs at liquid nitrogen temperatures only about one-fourth as much hydrogen as does ordinary graphite.

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