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The Adsorption of Carbon Dioxide on Carbon Solids

Part 1 - Graphite and Diamond at 0°C

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Abstract: The high-temperature physical adsorption of carbon dioxide ($\ll 1\%$ coverage) was measured on a number of relatively well defined carbon solids. The results provide an experimental means to differentiate between two arrays of adsorption sites that originate in the strong anisotropy of the graphite structure.

The adsorption isotherms at 0°C indicate two distinct regions of surface coverage that are separated by a wide plateau. The adsorption at very low pressures (< 0.01 torr) is considered to correspond to high-energy adsorption on an array of edge carbon atoms in the prism faces; the additional adsorption at higher pressures takes place at sites of lesser energy in the more abundant basal planes. Similar behavior was observed for graphitized carbon black FT (2700°C), mineral graphite, an annealed pyrolytic graphite, and a deashed heat-treated (1500°C) coconut charcoal. In contrast, the adsorption of carbon dioxide on purified natural-diamond fragments followed a simple Langmuir isotherm compatible with the known isotropic structure of diamond.

The amounts adsorbed expressed per unit area bring out similarities among the carbon solids that are characteristic of graphite. The large adsorption on the coconut charcoal appears due only to the large area that is essentially basal plane in behavior. There is evidence that the pyrolytic graphite has a porosity that may be invaded more completely by carbon dioxide than by krypton.

INTRODUCTION

In view of the well-known strongly anisotropic properties of graphite (1), the boundary surfaces of graphitic solids should present two arrays of adsorption sites. One array is located in the abundant basal planes; part of these sites originate in the discontinuity of the crystal lattice associated with the formation of a surface, and another part is due to defects such as warping of the basal plane. The second array of sites is located in the prism faces of the graphite crystal, where the constituent carbon atoms are also the edges of the basal planes. If the surface energy contained in these edge atoms is not entirely self-compensated in some way by bond isomerism (2), much stronger adsorption sites relative to the basal plane should be present (due ultimately to differences in the electronic states of the edge carbon atoms). Different specimens of graphite could then vary in surface properties according to the proportion of basal plane and prism faces that are present.

The basic assumption here, of course, is that the anisotropic properties of the crystal extend into the boundary surface. This is a likely possibility, and it is suggested in this report that the high-temperature physical adsorption ($\sim 0^\circ\text{C}$) of carbon dioxide may provide an experimental means to differentiate between the two sets of adsorption sites on the total boundary surface of graphitic carbons. It is necessary to combine a high temperature and low pressure (below 1 torr) in order that the surface coverage be sufficiently low to discriminate between the adsorption sites. It is also essential that the experimental conditions permit a physical adsorption process to be the dominating interaction.

That carbon dioxide is a desirable adsorbate to make the differentiation may be seen from two considerations.

1. The first consideration is that, on the one hand, the diameter attributed to this molecule is 3.53\AA as determined from spectroscopic measurements (3); 3.23\AA from the van der Waals equation of state of the gas, 3.40\AA from thermal conductivity theory, and 3.34\AA from viscosity determination. These coincide fairly closely with the separation of basal planes in crystalline

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graphite (3.347Å). On the other hand, the distance of closest approach of carbon atoms in the basal plane is 1.42Å, and the potential field of the surface which contributes to the adsorption of a gas is concerned with carbon separations of 1.42Å (ortho), 2.46Å (meta), and 2.84Å (para). Because the long axis of the carbon dioxide molecule is a good fit in the prism face, and a misfit in the basal plane, the distances of closest approach between the prism faces and the gas are smaller; this results in a greater van der Waals attraction at the prism face than at the basal plane.

2. An equally important consideration in the selection of carbon dioxide is the polarizability, α . At right angles to the C—C bond, α_{\perp} is very small, and parallel to the bond α_{\parallel} is 3.42×10^{-24} cm³ (4). Moreover, the carbon dioxide molecule is anisotropic; at right angles to the linear molecule $\alpha_{\perp} = 1.97 \times 10^{-24}$ and along the molecule $\alpha_{\parallel} = 4.01 \times 10^{-24}$ cm³. Accordingly, the average value for α_{ij} to be used in the summation of interactions between gas molecule and surface will show greater values for the prism faces than for the basal planes.

As a result of both considerations, the van der Waals energy of attraction when summed over the required distances,

$$-\sum_{i,j} \frac{C_{ij}}{r_{ij}^6},$$

will be much larger for the prism faces than for the basal planes, the polarizability factor being included in the constant C_{ij} .

The total adsorption of gas on two arrays of sites that differ greatly in energy should be reflected in the shape of the isotherm. It is necessary, of course, to employ pressures of a sufficiently wide range to span the anticipated coverages. When Langmuir adsorption is expressed in the form

$$\theta = \frac{bp}{1 + bp},$$

where θ is the coverage, p is the pressure, and b is a constant containing the energy terms in an exponential form, the influence of b on the relative shape of the isotherms is shown in the top half of Fig. 1. If two arrays of sites exist of $b = 1$ and $b = 1000$, the total isotherm should have the

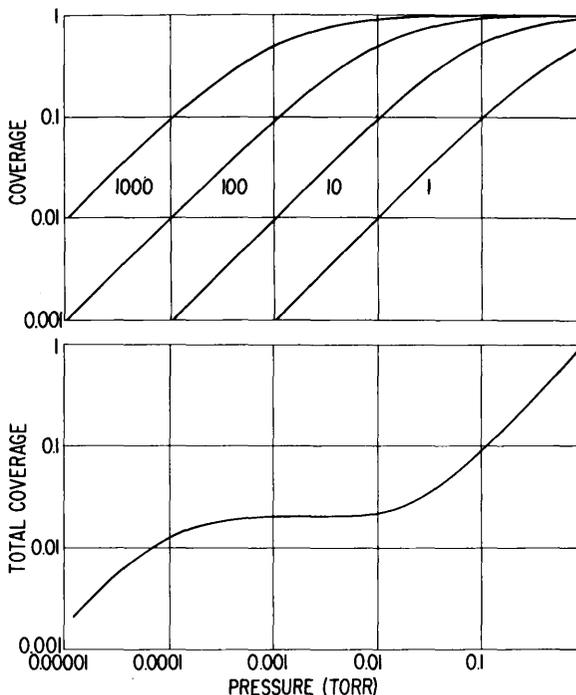


Fig. 1 — Top: Langmuir isotherms of different values of b (energies of adsorption). Bottom: Summation of two isotherms with $b = 1$ and $b = 1000$ on surfaces of equal area.

shape shown at the lower part of Fig. 1. A similar dependency of adsorption on crystal planes was pointed out a number of years ago by Cremer (5) in connection with a catalyst problem.

EXPERIMENTAL PROCEDURE

The volumetric adsorption equipment included metal valves (Granville-Phillips, Bakeable, Type C) mounted securely on a slotted angle beam in a vertical position. The glass connections were constructed so as to provide the flexibility required in manipulating the metal valves with a torque wrench. The pressure measurements were made with a thermocouple gage (RCA 1946) thermostated at $28.0 \pm 0.1^\circ\text{C}$. The controlled current through the gage (about 60 milliamperes) was frequently checked and adjusted so that the emf reading in vacuum (below 10^{-5} torr) was 10.030 millivolts. The recorder used in making all readings had a range of 1 millivolt full scale of 100 divisions, so that a difference of 1 microvolt was

observable. The thermocouple heating current was derived from a high-capacity storage battery (2.5 volts, Eveready T-2600, National Carbon Company) and the current was manually adjusted before each reading to the value required in high vacuum to give the reference emf. The recorder was calibrated at regular intervals against the bucking emf of a standard potentiometer.

A calibration was made for each gas using two McLeod gages with overlapping pressure ranges. The mercury vapor was trapped by a U-tube immersed in an alcohol-Dry Ice bath. The heights of the mercury levels of the McLeod gage were read relative to a fixed mark scratched on the glass near the end of the closed capillary. A Gaertner cathetometer solidly mounted on a cement block was used, and the measurements reported to 0.01 mm. The usual trials and tribulations attendant in McLeod gage operation were encountered, but these could be minimized by frequent outgassing of the gages. The thermocouple calibrations for carbon dioxide and krypton have shown good reproducibility over several years of operation using the above described procedure.

When adequately outgassed, the system without the sample held a vacuum below 10^{-5} torr for periods longer than those used in sample operations. The pumping system included a Consolidated Vacuum all-glass diffusion pump which when charged with Convelex-10 produced a vacuum well below 10^{-6} torr without a liquid nitrogen trap.

MATERIALS

The five materials that were used are listed in Table 1. Three were graphite specimens: FT carbon black (2700°C), a purified mineral graphite, and an annealed sample of pyrolytic graphite. Also, an acid-washed sample of coconut shell charcoal was prepared and heated in vacuum to 1500°C. The analyses of these materials for residual hydrogen are given in the table, this constituent being the principal impurity. The surface areas are also given in the table, that of charcoal and FT carbon having been determined with nitrogen (16.2\AA^2 cross-sectional area) at 77.4°K and the remaining three with krypton (17.2\AA^2 cross-sectional area) at 77.4°K. The

TABLE I
Properties of the Materials Investigated

Material	BET* Surface Area (m ² /g)	H Content† (wt-%)	Carbon Content † (wt-%)
Coconut shell charcoal‡	900	0.006	99.99
FT carbon (2700°C)§	10	0.00	100.0
Mineral graphite¶	0.74	0.00	100.0
Pyrolytic graphite**	0.029	0.00	100.0
Diamond fragments††	0.045	0.00	99.92

*S. Brunauer, P.H. Emmett, and E.T. Teller, *J. Am. Chem. Soc.* **60**: 309-319 (1938).

†Kindly supplied by R. A. Paulson of the Analytical Chemistry Division, National Bureau of Standards.

‡Acid-washed with HCl and HF and heated to 1500°C in vacuum.

§Kindly furnished by Dr. Walter Smith, Cabot Carbon Company.

¶Acid-washed with HCl-HF and heated to 1000°C in argon.

**Kindly furnished by Dr. R. J. Diefendorf, General Electric Research Laboratories.

††Kindly supplied by the National Bureau of Standards.

vapor pressure of krypton was determined and agreed with that reported by Fisher and McMillan (6).

The samples, contained in quartz or Vycor tubes, were attached to the Pyrex apparatus with graded seals; the weights ranged from 1 to 20 grams. The outgassing was conducted at elevated temperatures (up to 900°C) until the gas evolution from the hot samples decreased to about 6 nanomoles per hour.

The sample of natural diamond fragments (19.5 grams) was acid-washed, and the final washings gave no detectable sulfide or hydroxide tests. The indicated surface area (BET with krypton) actually decreased from 530 to 450 cm² as a result of this treatment.

All pressure measurements with the sample below room temperature were corrected for thermal transpiration. The modified procedure of Takaiishi and Sensui (7) was used for both krypton and carbon dioxide. Both of these gases were of spectroscopic grade supplied by the Air Reduction Company, Inc.

EXPERIMENTAL RESULTS

The adsorption of CO₂ at 0°C on graphitized FT carbon black is shown in Fig. 2. At pressures

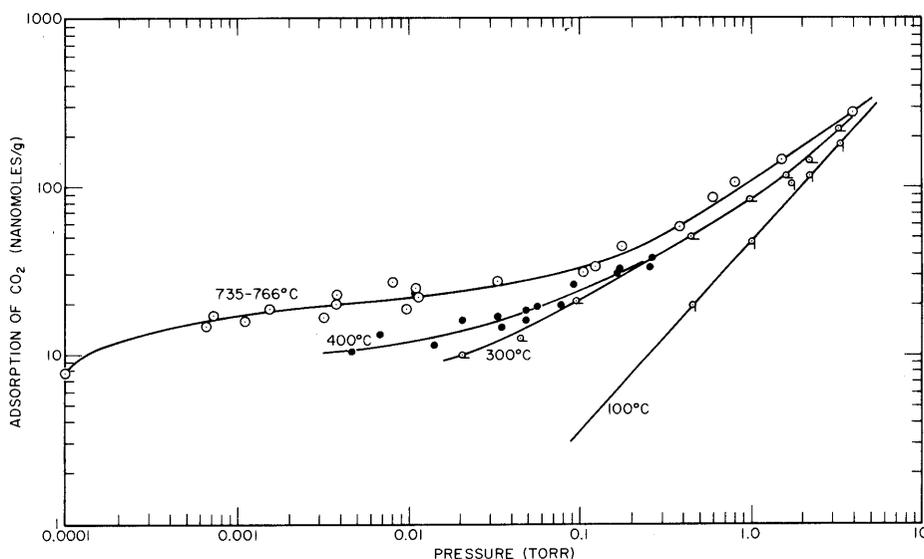


Fig. 2 — Adsorption isotherms of CO_2 at 0°C on graphitized FT carbon (2700°C). The exposure to the CO_2 was at 22.5°C and 1.5 torr for 3 hours; subsequent outgassing was at the temperature indicated for four days before cooling to 0°C .

above 1 torr, a linear isotherm was obtained as shown by the approach of the observed isotherm to a slope of unity. At still higher pressures linear isotherms for this graphitized carbon black have been reported at 0°C between 20 and 400 torr by Deitz, Carpenter, and Arnold (8) and between 150 and 350 torr by Myers and Prausnitz (9). Linear isotherms were also reported by Constabaris, Singleton, and Halsey (10) for neon, argon, and krypton on a similar material, P33 carbon black (2200°C).

Below 1 torr the adsorbed carbon dioxide becomes increasingly less dependent on pressure over several decades. The development of a plateau in the isotherm occurs only after the sample has been outgassed at a suitably high temperature. This is illustrated by the four groups of points shown in Fig. 2. All were determined after exposure of the sample of FT carbon to CO_2 at 22.5°C and 1.5 torr for 3 hours. The isotherm at the lower right was obtained after the sample was outgassed at nearly 100°C for four days and then cooled at 0°C . Subsequently, the outgassing was conducted at temperatures of 300, 400, and 730°C . The approach to the plateau appears to be asymptotic. The adsorption data given in Table 2 were obtained after outgassing at about 750°C .

Similar behavior is shown in Fig. 3 for the adsorption of CO_2 at 0°C on a pyrolytic graphite. The solid points were obtained after the sample of 24.25 grams was outgassed at 835°C for two days; the points in open diamonds are for an independent run after outgassing at 675°C for ten days. The results at pressures above 0.1 torr define a linear isotherm, and the results at lower pressures level off in a manner similar to those for the graphitized FT carbon black in Fig. 2. The adsorption data for pyrolytic graphite are given in Table 3.

The isotherm for mineralogical graphite is given in Fig. 4. The outgassing of this material (8.712 grams) was rather time consuming. Eventually, a gas evolution of approximately 6 nanomoles per hour was reached with the sample at 750°C and maintained at this level for several days. The adsorption data are given in Table 4.

The diamond fragments, after acid-washing as mentioned above, were outgassed at 480°C and the rate of gas evolution from the hot sample readily decreased to 6 nanomoles per hour. Two independent sets of measurements at 0°C were made six months apart. The isotherm shown in Fig. 5 includes points obtained by both adsorption and desorption. The data for both sets of measurements are given in Table 5.

TABLE 2
 Adsorption of CO₂ at 0°C on
 FT Carbon Black (2700°C)*

Pressure (torr)	Adsorption (nanomoles/g)	Adsorption (nanomoles/m ²)
Series 4 – Outgassed at 750°C		
0.140	33.7	3.37
0.656	84.4	8.44
0.862	104	10.4
1.56	142	14.2
4.08	273	27.3
Series 5 – Outgassed at 750°C		
0.0427	18.4	1.84
0.1125	23.2	2.32
0.0354	20.3	2.03
0.0114	18.3	1.83
0.00388	16.7	1.67
0.00150	15.3	1.53
0.00066 ₃	14.5	1.45
Series 9 – Outgassed at 745°C		
0.392	57.0	5.7
0.177	44.6	4.5
0.0815	34.2	3.4
0.0370	30.8	3.1
0.0169	29.2	2.9
0.0081 ₃	27.0	2.7
Series 11 – Outgassed at 735°C		
0.0351	23.8	2.4
0.0114	21.1	2.1
0.00379	19.9	2.0
0.00155	18.2	1.8
0.00073	17.0	1.7
Series 24 – Outgassed at 766°C		
0.00010	08.0	0.8
0.00907	18.6	1.9
0.00322	16.7	1.7
0.00115	15.7	1.6
0.00067	14.8	1.5

*Plotted in Fig. 2.

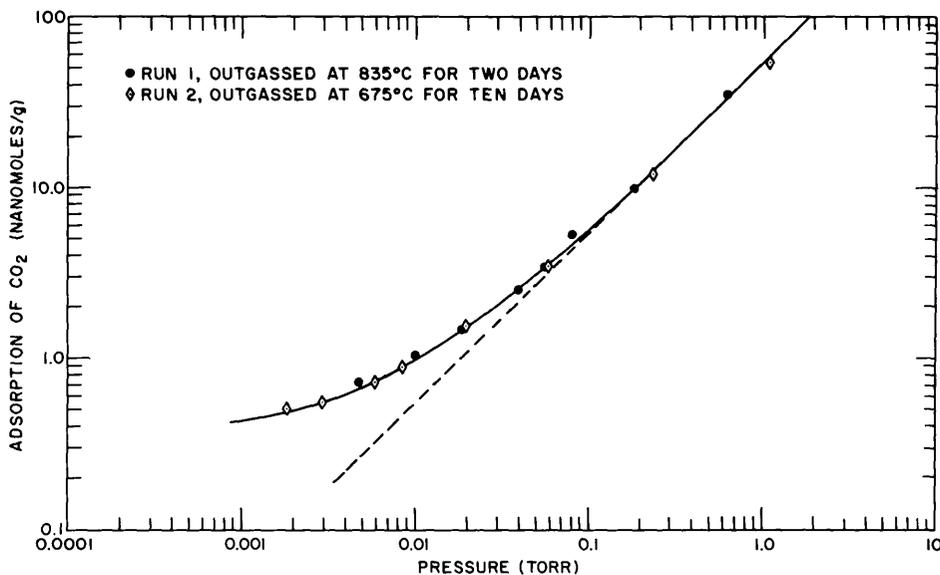
Fig. 3 — Adsorption of CO₂ at 0°C on an annealed pyrolytic graphite

TABLE 3
Adsorption of CO₂ at 0°C
on a Pyrolytic Graphite

Pressure (torr)	Adsorption* (nanomoles/g)	Adsorption (nanomoles/m ²)
Outgassed at 835°C for Two Days		
0.0048	0.72	25
0.0102	1.05	36
0.0191	1.47	50
0.0398	2.5	86
0.0564	3.5	120
0.082	5.2	178
0.184	9.9	339
0.630	35.8	1230
Outgassed at 675°C for Ten Days		
0.00187	0.51	17
0.00298	0.56	19
0.00596	0.73	25
0.00856	0.88	30
0.0196	1.50	51
0.0583	3.54	121
0.235	12.9	442
1.13	54.7	1870

*Plotted in Fig. 3.

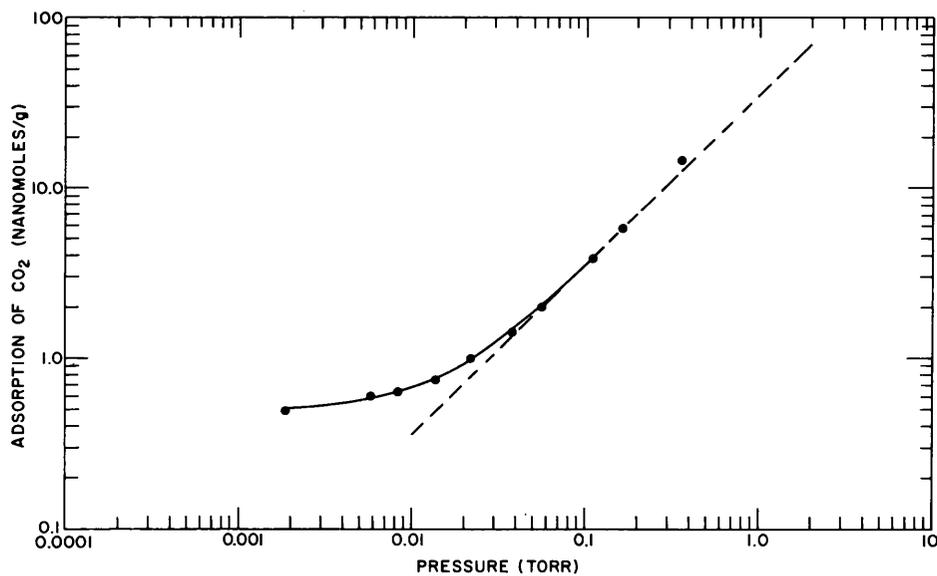


Fig. 4 — Adsorption of CO₂ at 0°C on purified mineral graphite outgassed at 750°C

TABLE 4
Adsorption of CO₂ at 0°C on Purified Mineral
Graphite Outgassed at 750°C

Pressure (torr)	Adsorption* (nanomoles/g)	Adsorption (nanomoles/m ²)
0.00186	0.49	0.66
0.00572	0.61	0.82
0.00812	0.63	0.85
0.0137	0.76	1.03
0.0218	1.01	1.36
0.0371	1.45	1.96
0.0551	2.05	2.77
0.110	3.88	5.24
0.161	5.91	7.98
0.360	14.8	20.0

*Plotted in Fig. 4.

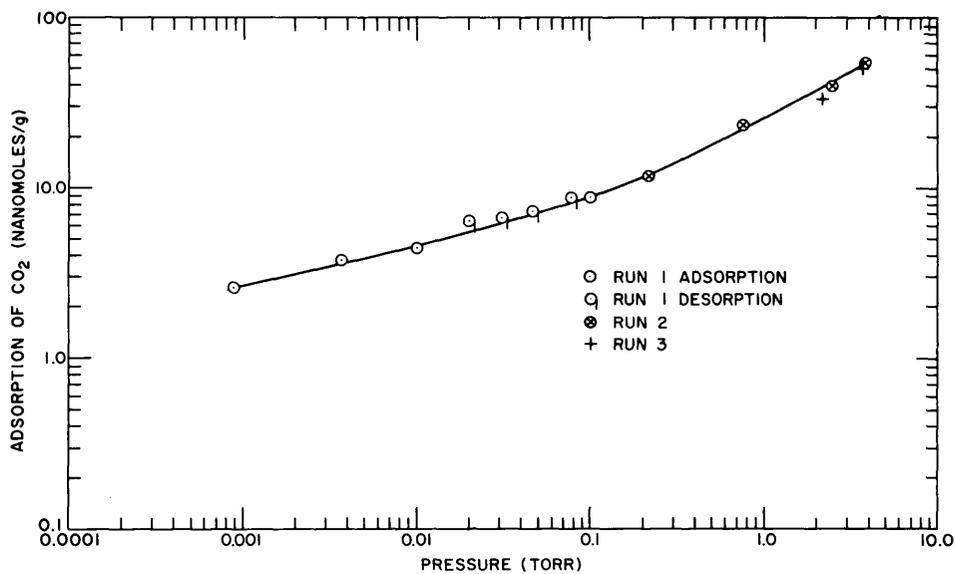


Fig. 5 – Adsorption of CO₂ at 0°C on purified diamond fragments outgassed at 480°C (see Fig. 12 for Langmuir plots)

TABLE 5
Adsorption (and Desorption) of CO₂
on Diamond Fragments at 0°C

Pressure, p (torr)	Adsorption, N (nanomoles/g)	Adsorption (nanomoles/m ²)	p/N
Run 1			
0.00088	2.6	57	0.00034
0.0037	3.8	83	0.00098
0.0100	4.5	99	0.0022
0.099	8.9	195	0.0112
0.078	8.7	193	0.0089
0.046	7.3	160	0.0063
0.033	6.7	148	0.0048
0.020	6.4	142	0.0031
Run 2 – Six Months Later			
0.073	9.9	220	0.0073
0.426	16.3	360	0.026
0.68	16.6	365	0.041
1.08	19.3	420	0.056
2.82	20.1	440	0.140

Fig. 6 — Time-dependent adsorption of CO_2 on acid-washed heat-treated (1500°C) coconut shell charcoal. The dose numbers denote successive doses of CO_2 .

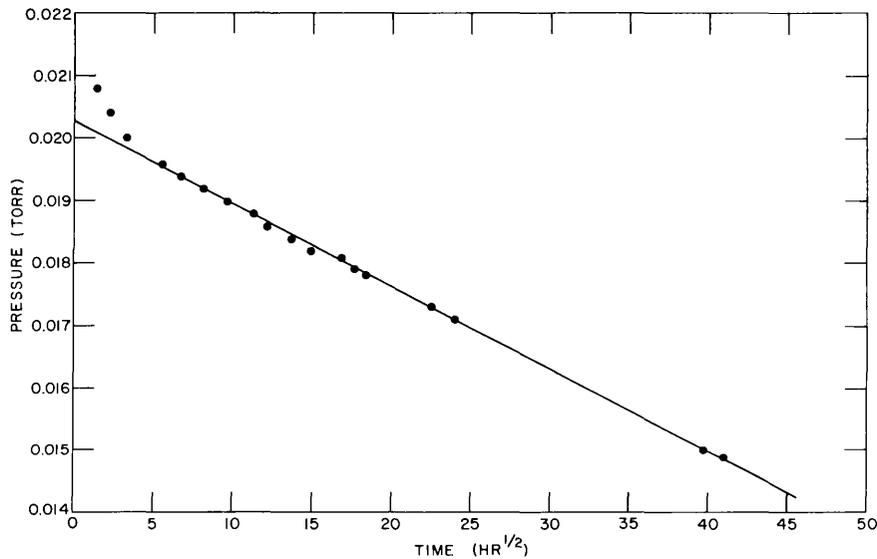
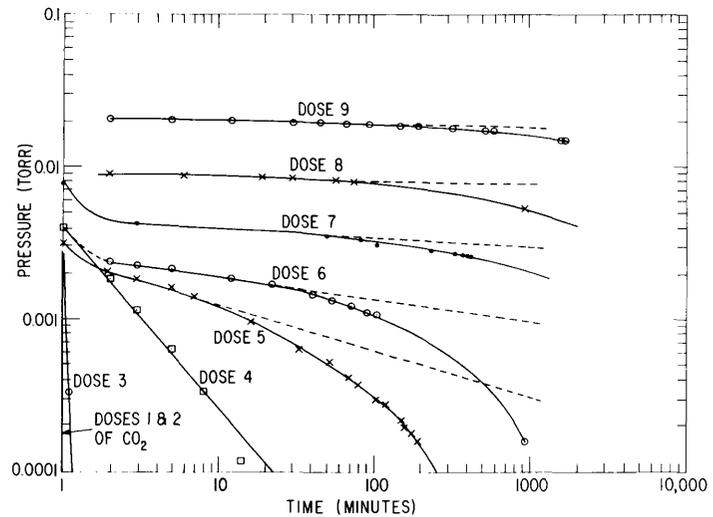


Fig. 7 — Pressure change of CO_2 during adsorption of dose 9 on charcoal and followed for 28 hours (see Fig. 6)

The adsorption of carbon dioxide on the sample of treated coconut shell charcoal (Fig. 6) exhibited a very slow approach to a steady state. Although this behavior was most pronounced for the charcoal, the graphites also behaved similarly for the points on the isotherm at pressures below the plateau region. For these samples, too, a somewhat greater time dependence was found in the approach to a steady state than in the region of higher pressures above the plateau. The pressure-time dependence for nine successive doses of carbon dioxide on the charcoal at 0°C is shown

in Fig. 6. The adsorption of the first three doses took place so rapidly that the pressure change could not be followed. The succeeding doses were adsorbed more slowly, and the kinetics appeared to follow various schemes. For example, the pressure changes following dose 9 were closely proportional to $\sqrt{\text{time}}$ for the 28 hours during which the observations were made. This behavior is illustrated in Fig. 7. On the other hand, dose 4 followed a linear dependence on time, as shown in Fig. 6. The adsorption results are summarized in Table 6.

TABLE 6
Adsorption of CO₂ on Coconut Shell Charcoal Acid-Washed
and Heated in Vacuum to 1500°C

Dose No.	Dose (μ moles)	Time Observed (min)	Initial Pressure (torr)	Final Pressure (torr)	Adsorption at Final Pressure (nanomoles/g)	Adsorption at Final Pressure (nanomoles/m ²)
1	0.668	<1	0.0676	<0.0001	80	0.089
2	2.194	<1	0.222	<0.0001	342	0.38
3	2.690	1-5	0.272	<0.0001	663	0.74
4	6.050	1-47	0.612	<0.0001	1390	1.54
5	3.083	1-192	0.312	0.00016	1750	1.95
6	2.273	2-933	0.230	0.00016	2030	2.25
7	2.909	1-412	0.294	0.0026	2370	2.64
8	2.837	2-918	0.288	0.0054	2700	3.00
9	5.581	2-1680	0.565	0.0149	3360	3.73

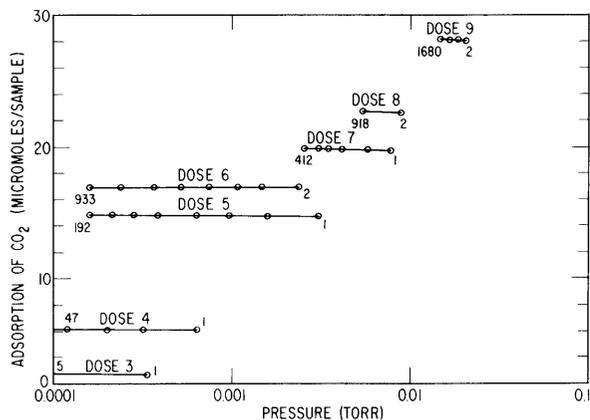


Fig. 8 — Adsorption of the charcoal during the designated time intervals (in minutes) as a function of the corresponding pressures

The amounts adsorbed at various times were calculated, and these are plotted in Fig. 8 as a function of pressure. The adsorption increased with time, but this is not evident in Fig. 8 due to the large scale required on the ordinate axis to cover all of the data. There is first a very rapid adsorption which is followed by much slower adsorption, and it is the pressure change due to the latter that is recorded in Fig. 6. The significance of this behavior is the main subject of Part 2 of this series of reports, which report is concerned with diffusion-controlled aspects of the adsorption process. The weight of the charcoal sample was 8.374 g, which corresponded to an

area of about 7500 m². A more detailed study of the rates of adsorption between 0 and 100°C is concerned with sample weights between 1 and 50 grams in order to reach both lower and higher surface coverages.

DISCUSSION

The experimental adsorption isotherms for carbon dioxide on adequately outgassed graphite solids have a shape suggested by the simplified model given in the bottom half of Fig. 1. At pressures above the plateau region, the adsorption process at 0°C is controlled by a physical adsorption on the sparsely covered and high-area basal plane. A high mobility of the carbon dioxide molecule on the basal planes will rapidly populate the prism faces, which present a greater heat of adsorption. The heats of adsorption for coverages above the plateau region are only somewhat larger than the heats of vaporization of liquid carbon dioxide. The latter (11) are plotted for various temperatures in Fig. 9, where the rapid drop between 0°C and the critical temperature may be seen. The isosteric heats of adsorption of carbon dioxide on pyrolytic and mineralogical graphites were estimated. Qualitatively, the heats at higher coverages approached a constant value as the linear isotherm region was reached. At lower coverages the heats were larger. However, the uncertainty then became large due to the insufficient precision in determining the adsorption

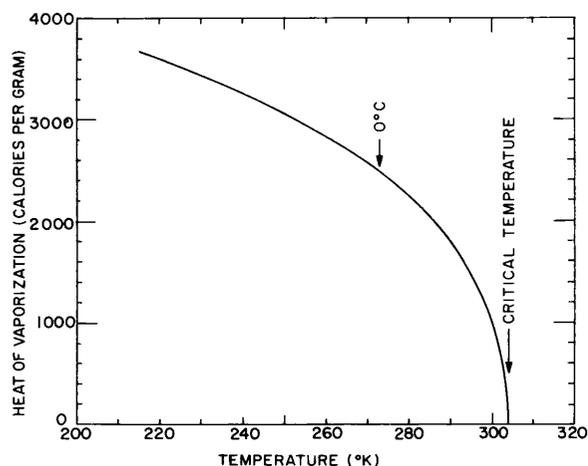


Fig. 9 — Heats of vaporization of CO₂ at pressures corresponding to the vapor pressure of the liquid

isotherms at different temperatures in the plateau region. It is readily apparent that in this region a small change in the amount adsorbed corresponds to a large pressure change and, therefore, to a large change in the calculated isosteric heat. Further discussion of the heats of adsorption of carbon dioxide is postponed until data are obtained with a new apparatus now being designed with more precision at the lower pressures. The literature values for the heats of adsorption of carbon dioxide on graphite are given in Table 7.

In order to express the adsorption per unit surface, it is necessary to have the cross-sectional

area (σ) of an adsorbed CO₂ molecule at 0°C. There is considerable uncertainty in the value to be used in this investigation, as well as in previous studies at -78°C. Using the molar volume of the liquid (11), and assuming hexagonal close-packing in both the liquid and the adsorbed two-dimensional layer, the calculated values of σ_{CO_2} are given by the solid line of Fig. 10, which covers temperatures from -50°C to the critical point. The value of $\sigma_{CO_2} = 20\text{\AA}^2$ corresponds to the cross-sectional area of carbon dioxide at 0°C.

The adsorption for the five carbon solids is expressed in Fig. 11 as nanomoles of CO₂ per square meter. The graphitized FT carbon black (B in Fig. 11), the coconut charcoal (F), and the mineralogical graphite (A) approach a common plateau at the lower pressures ranging between 1 and 2 nanomoles per m². A monomolecular layer of liquidlike carbon dioxide at 0°C would require about 8300 nanomoles per m²; thus, the plateau for these three carbon solids corresponds to a fractional coverage in the range 0.0001 to 0.0002. The similarity of coconut shell charcoal when expressed on a *per unit area basis* to mineralogical graphite and to FT graphitized carbon black at pressures below 0.01 torr emphasizes the dependence of the adsorption on basal plane area alone. The adsorption corresponding to the plateau when expressed per gram of charcoal is 1800 nanomoles per gram. This corresponds to an average fractional coverage of 0.00025.

TABLE 7
Heat of Adsorption of CO₂

Sample	Measurement	Temperature (°C)	Heat of Adsorption (kcal/mole)	Ref.
Sterling FT (2700°C) Sterling FT (3100°C)	Calorimetric	-79	4.8-6 4.4-6	12
Sterling FT (2700°C)	Isotherm at const. spreading pressure	0 36.07	2.978 2.956	9
Sterling FT (2700°C)	Isosteric heat	0 and -5	2.52	8
Pyrolytic Graphite	Isosteric heat	0 and 21	1.6	This report

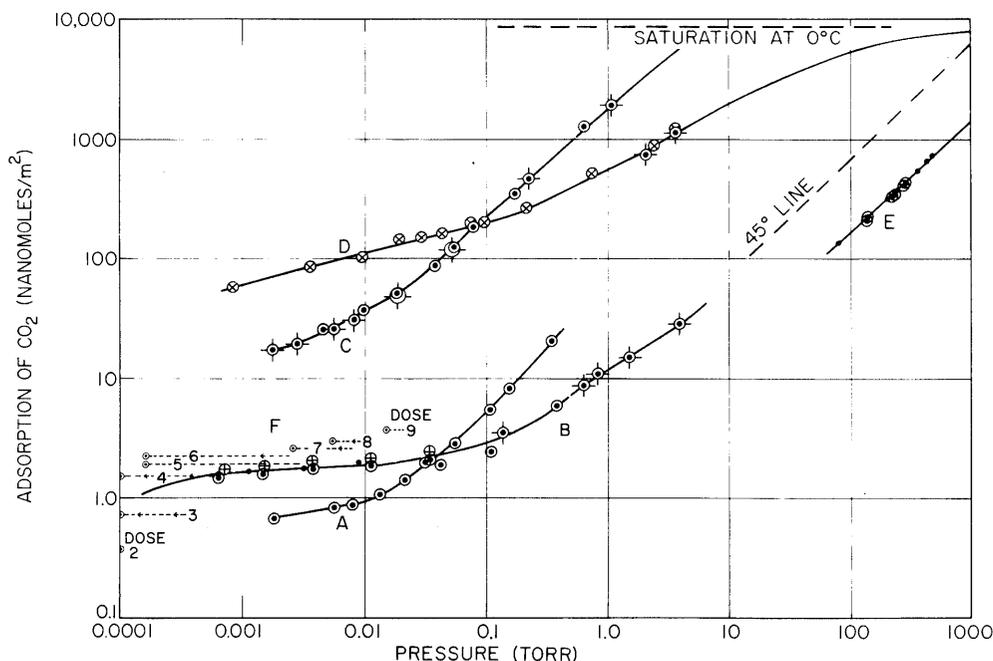


Fig. 11 — Adsorption of CO₂ per unit area on the five samples: (A) mineral graphite, (B) FT carbon black, (C) pyrolytic graphite, (D) diamond fragments, (E) previous observations (8,9), and (F) coconut shell charcoal

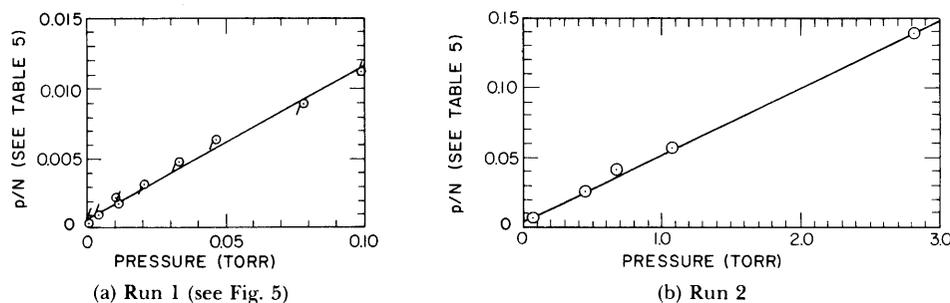


Fig. 12 — Langmuir plots for adsorption of CO₂ on diamond fragments

degree of freedom. Measurements are now in progress to determine whether the carbon dioxide molecule can, under favorable conditions, actually intercalate the structure of pyrolytic graphites and, if so, whether intercalation occurs to a significant extent in pyrolytic graphite in comparison to any intercalation in some mineral graphites.

CONCLUSIONS

The similar behavior of the coconut shell charcoal, graphitized FT carbon black, and a mineral

graphite when the adsorption of carbon dioxide on their surfaces is expressed on a per-unit-area basis may be a significant observation. The greater part of the carbon dioxide adsorption on the charcoal is thus attributed to adsorption on the basal plane structure. Moreover, the results for diamond suggest that should it be possible to combine large BET area and surface aliphatic C—C bonds (stabilized perhaps as in diamond), there would be formed a carbon adsorbent of a greatly enhanced capacity. It is suggested that Saran charcoal, the pyrolysis residue of

polyvinylidene chloride, may be viewed as a step in such a synthesis. The most interesting properties of a number of partially pyrolyzed polymers in the adsorption of carbon dioxide at -78°C have been described by Kipling *et al.* (17).

The system studied in this report is one of general occurrence, where an anisotropic adsorbate interacts with a surface of a solid having anisotropic properties. In all likelihood the anisotropy of the solid extends into the boundary surface, and the composition of the boundary will vary with those pretreatments that influence the crystallization process of the solid. This may or may not be dependent on an impurity which may also be present in the gas-solid interface. A non-uniform surface, therefore, is a natural consequence of inherent anisotropy of the adsorbent. Incidentally, the commercial solid adsorbents have pronounced anisotropy in the crystallites of which they are composed.

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REFERENCES

- Ubbelohde, A.R., and Lewis, F.A., "Graphite and Its Crystal Compounds," Oxford:Clarendon Press, first edition, 1960
- Coulson, C.A., 1959 Proc. Conference on Carbon, 215-19
- Bowen, H.J., *et al.*, "Table of Interatomic Distances and Configuration in Molecules and Ions," Special Publication 11, London:Chemical Society, 1958
- Lippincott, E.R., and Stutman, J.M., *J. Phys. Chem.* **68**: 296-2940 (1964)
- Cremer, E., *Monatsh. Chem.* **77**:126-133 (1947), *J. chim. phys.* **46**:411-419 (1949)
- Fisher, B.B., and McMillan, W.G., *J. Phys. Chem.* **62**:494-495 (1958)
- Takaishi, T., and Sensui, Y., *Trans. Faraday Soc.* **59**:2503-2514 (1963)
- Deitz, V.R., Carpenter, F.G., and Arnold, R.G., *Carbon* **1**: 245-254 (1964)
- Myers, A.L., and Prausnitz, J.M., *Trans. Faraday Soc.* **61**: 755-764 (1965)
- Constabaris, G., Singleton, J.H., and Halsey, G.D., Jr., *J. Phys. Chem.* **63**:1355 (1959)
- Bull. Intern. Inst. Refrigeration* **22**(No. 2):55-66 (1941), Appendix
- Spencer, W.B., Amberg, C.H., and Beebe, R.A., *J. Phys. Chem.* **62**:719-723 (1958)
- Amberg, C.H., Everett, D.H., Rutter, L.H., and Smith, F.W., *Proc. Second Intern. Congress Surface Activity*, New York: Academic Press, vol. 2, 1957, pp. 3-16
- Gregg, S.J., "The Surface Chemistry of Solids," London: Chapman and Hall, 1961, Table 2.4
- Emmett, P.H., and Brunauer, S., *J. Am. Chem. Soc.* **59**:1553 (1937)
- Livingston, H.K., *J. Colloid Sci.* **4**:447-458 (1949)
- Kipling, J.J., Sherwood, J.N., Shooter, P.V., and Thompson, N.R., *Carbon* **1**:321-328 (1964)
- Pickering, H.L., and Eckstrom, H.C., *J. Am. Chem. Soc.* **74**:4775 (1952)

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13. ABSTRACT <p>The high-temperature physical adsorption of carbon dioxide (<<1% coverage) was measured on a number of relatively well defined carbon solids. The results provide an experimental means to differentiate between two arrays of adsorption sites that originate in the strong anisotropy of the graphite structure.</p> <p>The adsorption isotherms at 0°C indicate two distinct regions of surface coverage that are separated by a wide plateau. The adsorption at very low pressures (<0.01 torr) is considered to correspond to high-energy adsorption on an array of edge carbon atoms in the prism faces; the additional adsorption at higher pressures takes place at sites of lesser energy in the more abundant basal planes. Similar behavior was observed for graphitized carbon black FT (2700°C), mineral graphite, an annealed pyrolytic graphite, and a deashed heat-treated (1500°C) coconut charcoal. In contrast, the adsorption of carbon dioxide on purified natural-diamond fragments followed a simple Langmuir isotherm compatible with the known isotropic structure of diamond.</p> <p>The amounts adsorbed expressed per unit area bring out similarities among the carbon solids that are characteristic of graphite. The large adsorption on the coconut charcoal appears due only to the large area that is essentially basal plane in behavior. There is evidence that the pyrolytic graphite has a porosity that may be invaded more completely by carbon dioxide than by krypton.</p>		

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
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Adsorption						
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Graphite						
Anisotropy						
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