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Surface Area Studies of Carbon-Carbon Dioxide Reaction

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THE heterogeneous gasification reactions of carbon are of considerable theoretical and industrial interest and have been the subject of extensive research in recent years. However, although a number of comprehensive kinetic studies have been reported (1, 5, 6, 9-11), little information has been developed that serves to clarify the physical mechanism of the reactions. For the carbon-oxygen reaction, Bowering and Crone (2) have approached this problem through a consideration of the internal surface developed during reaction and have shown that reactivity

can be correlated with data on the heat of wetting and change in apparent density of the carbon. Similarly, Gulbransen and Andrew (7, 8) have shown that the internal surface area of graphite increases markedly during reaction with both oxygen and carbon dioxide.

In the heterogeneous reactions of a porous solid such as carbon, the effective surface area undergoing reaction would be expected to exert considerable influence upon reaction rates over the temperature region where chemical reaction controls. Although reaction rate data for a given carbon can be correlated by means of the Langmuir type equation in which only concentration of

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This work was undertaken to determine the changes of internal surface area of carbon during gasification with carbon dioxide and to investigate the relationship between the areas and the gasification rates. Rod samples of gas-baked petroleum coke and graphitized base carbon were used in the investigation. The reaction rate of both carbons increases with reaction time up to approximately 10% weight loss, and this is paralleled by an increase in internal surface area. The reaction rate then becomes a constant as does essentially the internal surface area. By reacting a constant weight from both carbons at various temperatures, it is shown that the area developed is a function of the carbon and of the reaction temperature. Over the temperature range 900° to 1100° C., reaction rate data indicate active rate concentrations four times greater for the gas-baked than for the graphitized carbon. The results indicate that internal surface area is an important parameter in the characterization of carbons before and during the gasification reactions.

gaseous reactants and products are required, the correlation is of little assistance in predicting rate data for other carbons. It would appear to be of interest, therefore, to determine what correlation exists between reaction rate and changes in surface area during reaction and also between reaction rate and differences in surface area for different carbons. For initial studies along these lines, the carbon-carbon dioxide reaction has been chosen because it is believed to be the simplest of the heterogeneous gasification reactions of carbon.

APPARATUS

The apparatus used in the reaction rate studies is shown diagrammatically in Figure 1. The main section of the porcelain reactor tube was heated by means of a high temperature Globar furnace with automatic temperature control capable of maintaining furnace temperature within $\pm 2^\circ$ C. Below the main furnace, a 9-inch resistance furnace was added to provide preheat to the incoming gas. This section of the reactor was packed with broken porcelain chips and maintained at approximately 900° C.

Mounted concentrically in the reaction tube was a 22-inch ceramic tube ($\frac{1}{2}$ -inch outside diameter by $\frac{2}{16}$ -inch inside diameter) held in place by the porcelain chips in the preheater section. The upper end of this tube was ground to fit ceramic cones attached to the lower end of the carbon samples, thus ensuring exact centering of the carbon sample and producing a continuous surface with the minimum distortion of the gas flow pattern past the sample.

Each carbon sample was machined from $\frac{5}{8}$ -inch rods to the exact dimensions of 2 inches in length by $\frac{1}{2}$ inch in diameter. A ceramic cone was cemented to the bottom, and a $\frac{1}{8}$ -inch inside diameter $\frac{1}{2}$ -inch outside diameter ceramic disk was cemented to the top of the sample, as shown in Figure 1. One end of an $18 \times \frac{1}{8}$ inch diameter ceramic rod was cemented into the ceramic disk and the other connected to a Roller-Smith torsion-type balance. The latter permits weighing of the sample during reaction with a precision of ± 0.01 gram up to temperatures of 1200° C.; above this temperature the precision decreases progressively to ± 0.02 gram at 1400° C. because of the high reaction rates.

The gas purification train of the system, not shown in Figure 1, consists of the following:

A tube packed with copper oxide and maintained at 450° C. to convert hydrogen to water vapor, a drying column packed with anhydrous magnesium perchlorate to remove water, a tube packed with copper wool and maintained at 650° C. to remove oxygen, and finally a drying tube packed with anhydrous magnesium perchlorate. For helium, argon, and nitrogen purification the full train was employed, but for carbon dioxide purification only the last two units were used. Gas flow rates were measured by means of calibrated rotameters with a precision of $\pm 1\%$.

Reaction temperature was measured by means of a calibrated platinum-platinum-10% rhodium thermocouple, protected by

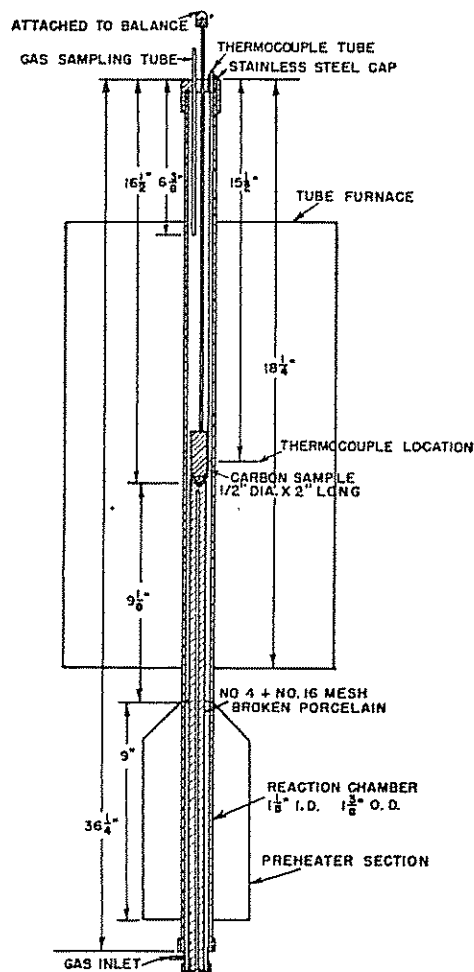


Figure 1. Cross Section of Reaction Chamber

means of a glazed ceramic tube extending into the reaction tube $\frac{1}{4}$ inch below the center of the carbon sample. Axial and radial temperature traverses made in the vicinity of the sample indicated that constant readings were obtained from 1 inch below to 1 inch above the location of the carbon sample. A similar traverse with and without preheat gas flowing showed no effect of gas flow over the range employed in this work and indicated satisfactory preheating of the gas. Although not employed during actual rate studies, because it interfered with weight determinations, several tests were previously made for the graphite-steam reaction (14) with a thermocouple and protecting tube replacing the usual sample suspension tube. During reaction at

900° and 1100° C. the agreement between the temperature at the center of the carbon sample and that read by the thermocouple in its normal position outside the sample was within 2° C.

Heat transfer calculations using the following equation predict a Δt of 2.5° C. for the graphite-steam reaction at 1100° C.

$$Q = h_r A \Delta t$$

where Q is the heat which must be transferred to the carbon sample per unit of time to sustain the endothermic reaction; h_r is the heat transfer coefficient by radiation assuming an emissivity and absorptivity of 1; A is the external area of the carbon sample; and Δt is the temperature gradient from the sample to the tube wall.

In the graphite-carbon dioxide reaction, a Δt of 6° C. was calculated at 1100° C. The maximum temperature difference between the exterior of the graphite sample and the thermocouple was calculated to be about 12° C. for the gasification reaction at 1400° C. For the gas-baked carbon, with its greater reaction rate, the temperature difference was calculated to be about 15° at 1100° C. Hereafter, the temperatures reported are those read by the thermocouple. The only place where it was thought important to use the actual temperature of the reaction was in the Arrhenius plots. However, here the corrections produced a negligible effect on the apparent activation energy, certainly less than the accuracy with which it can be determined.

For surface area determinations, the standard B.E.T. apparatus and method (4) were employed using carbon dioxide, nitrogen, and argon as adsorption gases.

REACTANTS

Two types of carbon, a gas-baked carbon and an artificial graphite, used in this investigation were produced from the same batch of raw materials (furnished by the Speer Carbon Co. through the courtesy of H. W. Abbott) in the form of rods $\frac{1}{8}$ inch in diameter and 12 inches long. These rods were made by extruding a mixture of petroleum coke flour (60% through 200 mesh) and coal tar pitch. The gas baked carbon resulted from baking the extruded rods at a temperature of approximately 1000° C. for several weeks. The graphite rods were produced by graphitizing part of the gas-baked carbon rods at a temperature of approximately 2500° C. for about 12 hours. The porosity of the gas-baked carbon and graphite rods as determined from true and apparent specific gravity measurements were 24.4 and 26.0%, respectively, as reported by H. W. Abbott, Speer Carbon Co. The former was determined by grinding the samples to pass through a 200-mesh screen and using kerosene as the fluid in the pycnometer. Table I shows the over-all analyses of the samples on a moisture-free basis, and Table II shows spectrographic ash analyses of these samples.

The samples, $\frac{1}{2}$ inch in diameter and 2 inches long, were cut from these rods on a metal turning lathe to remove the outer $\frac{1}{16}$ -inch layer of carbon, because ash reportedly tends to concentrate near the surface and also because the possibility of a skin effect due to extrusion was suspected. Short $\frac{1}{8}$ -inch diameter holes were drilled in both ends to permit fastening of the ceramic cones and suspension rods. To test for the possible deposition of metal particles in the carbon pores during machining, a sample was washed in concentrated hydrochloric acid, then with distilled water until the washings were free of chloride ions, evacuated to 10^{-4} mm. of mercury at 150° C. for 24 hours, and reacted with carbon dioxide in the standard manner. No difference in reaction rate could be detected between the washed and unwashed samples, so it was assumed that either the deposition was negligible or that it had a negligible effect on reaction rate.

The gases used in the investigation were of the highest obtainable commercial purity. The carbon dioxide was of the "bone dry" grade and had a purity of 99.956% as listed by the Matheson Co. The helium, also from Matheson, had a listed purity of

Table I. Analyses of Gas Baked Carbon and Graphite Rods

	C, %	H, %	O + N, %	Ash, %
Gas-baked carbon	97.09	0.19	1.12	1.6
Graphite	99.23	0.03	0.44	0.3

Table II. Ash Analyses of Gas-Baked Carbon and Graphite Rods^a

a = absent
nd = not determined
X = first significant figure in per cent

Element	Gas-Baked Carbon	Graphite
V	0.00X	0.00X
Al	0.00X	0.000X
Ti	0.000X	0.00X
B	0.00X	0.00X
Ca	0.00X	0.00X
Ni	0.00X	0.000X
Cu	0.00X	0.000X
Fe	0. X	0.000X
Pb	0.00X	0.000X
Mg	0.0X	0.000X
Mn	0.00X	0.000X
Si	0.00X	0.00X
Na	0.00X	0.000X
Su	a	a
Cr	nd	nd
Cd	nd	nd
Mo	nd	nd

^a Analyses made by the National Spectrographic Laboratories, Inc. Cleveland, Ohio.

99.8% with the 0.2% impurity being mostly nitrogen. One cylinder of helium was analyzed by means of a conductivity-bridge apparatus; the purity was found to be 100%, with a precision of 0.02%. The nitrogen and argon, used in the adsorption studies, both had a purity of better than 99.8%.

PROCEDURE

Reaction Rates. The Globar reaction rate furnace was brought slowly up to temperature and allowed to remain at this temperature for at least 24 hours before making a run. The preheater, copper oxide, and copper furnaces were brought to operating temperature; hydrogen was passed through the copper furnace in order to remove any previously formed surface oxides, and the entire system then was flushed with helium at a rate of 190 cc. per minute for at least 1 hour before introducing the sample. (All flow rates are expressed at 760 mm. of mercury pressure and 20° C.) The flow of helium was maintained while the sample was preheated for the desired length of time, usually about 1 hour. Preliminary studies had shown that the duration of the preheating time in helium was not critical so long as the sample was given adequate time to attain temperature. When a run was started, the flow of preheating gas was stopped, and carbon dioxide was passed through the system at a rather high flow rate (4000 cc. per minute) for several minutes in order to flush out as rapidly as possible the remaining preheating gas. After this purge period, the sample weight was recorded and the carbon dioxide flow rate was adjusted to the desired value of 2200 cc. per minute. This flow rate placed the carbon dioxide flow pattern along the sample well within the viscous region with a Reynolds number of less than 200. The 2200 cc. per minute was selected as a compromise between higher flow rates, which might cause surface erosion of the sample, and lower flow rates, which would permit diffusional control of the reaction at too low a temperature or allow the production of too high a concentration of carbon monoxide. For the flow rate used, it was calculated that even for the highest reaction rates the maximum carbon monoxide concentration in the ambient gas stream was less than 0.1%. Sample weights were then recorded at time intervals sufficiently frequent to permit an accurate determination of the reaction rate curves. After reaction for the desired length of time, the carbon dioxide flow was stopped and helium was again passed through the system. The sample was slowly removed from the reaction chamber in such a manner as to permit it to cool to room temperature before coming in contact with air.

Low Temperature Adsorption. The samples for gas adsorption studies were weighed and sealed into the adsorption apparatus;

the entire system was evacuated at a temperature of 220° to 230° C. while the pressure in the system was maintained below 10^{-4} mm. of mercury. This outgassing was continued for approximately 12 hours or until the pressure rise, with vacuum pump shut off and heat still applied, was less than 10^{-3} mm. of mercury over a period of half an hour. The heating furnace was then removed and the sample allowed to cool to room temperature. The free space volume was determined with helium at

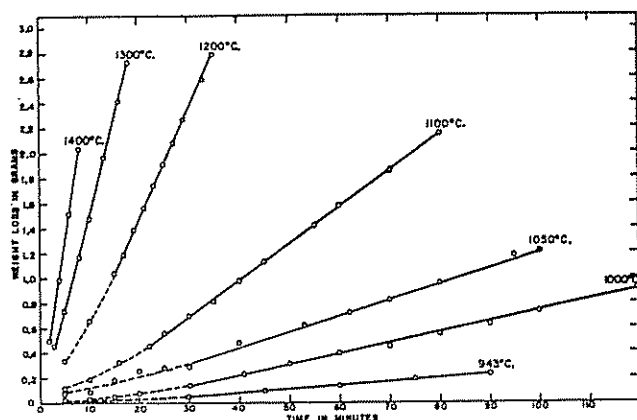


Figure 2. Reaction Curves for Graphite at Various Temperatures

room temperature. For carbon dioxide adsorption a bath consisting of a 50% solution of carbon tetrachloride in chloroform was used with dry ice. For nitrogen and argon adsorption, liquid nitrogen was used for the bath. The adsorption gases were all passed through an anhydrous magnesium perchlorate column prior to admission to the adsorption apparatus.

For nitrogen and argon adsorption, the saturation pressure, p_0 , of the adsorption gas at the bath temperature was obtained by admitting a copious amount of gas to the adsorption apparatus with the sample stopcock open. The final pressure was then at a ratio of $p/p_0 = 1$, or the saturation pressure of the gas. For carbon dioxide adsorption, the bath temperature was determined with an alcohol thermometer, and p_0 was determined from the vapor pressure-temperature curve. Since carbon dioxide sublimates at dry-ice temperature (-78° C.), it was necessary to extrapolate the liquid vapor pressure curve into the supercooled region in order to determine p_0 . This was accomplished by the use of the equation of Meyers and van Dusen (13).

RESULTS

Effect of Temperature on Reaction Rates of Carbon. The loss in weight of carbon samples at various temperatures, as a function of contact time in a flowing stream of carbon dioxide, is shown in Figures 2 and 3 for graphite and gas-baked carbon rods, respectively. Data were also obtained at 900° C. but are not shown because the rates were so low the curves have no significance on these coordinates. Runs carried out above 1200° C. were subject to experimental difficulty in that the sample weight changed measurably during weighing. Consequently, an average weight had to be used. Above 1400° C. for the graphite and above 1100° C. for the gas-baked carbon samples, the reaction was so violent that particles were blown completely out of the reaction chamber within 6 minutes after the start of the reaction.

In general, the reaction rate curves can be divided into three portions. Beginning at zero time there is first a curved section where the rate of weight loss increases rapidly; secondly, a straight section showing constant rate of weight loss; and thirdly, a section, not shown in Figures 2 and 3, where the rate of weight loss again increases and may be either straight or slightly con-

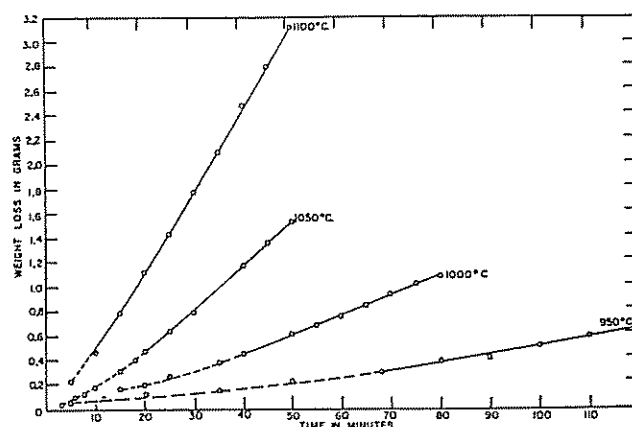


Figure 3. Reaction Curves for Gas-Baked Carbon at Various Temperatures

cave upwards. The initial curved section, shown as a dashed line on the reaction rate plots, is due in part to the increasing partial pressure of the carbon dioxide as helium is displaced both from the reaction chamber and from internal pores and also to the rapid increase in the sample's surface area during the initial stage of reaction. Calculations assuming piston flow and negligible back diffusion of helium suggest that the time required to displace helium from the annulus around the sample is less than 1 minute. However, the time required for the carbon dioxide to diffuse into the carbon and displace the helium in the internal capillary system is undoubtedly somewhat longer. The second section of the rate curve is a straight line, the slope of which is a measure of the actual rate of reaction between the carbon and the carbon dioxide under substantially equilibrium conditions. The third portion of the rate curve is not shown as it represents a

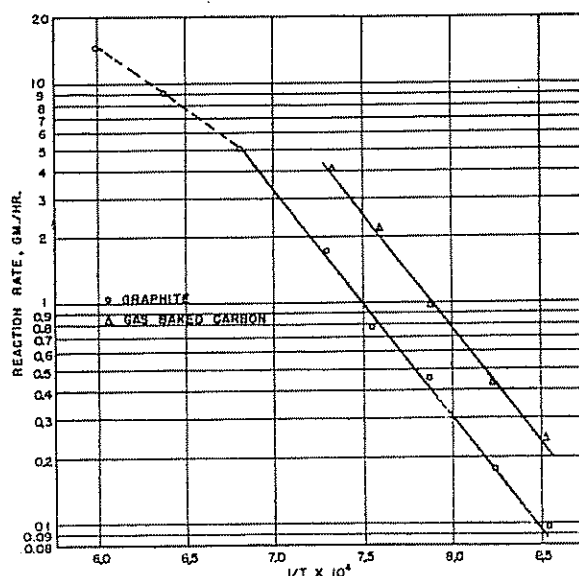


Figure 4. Arrhenius Plots for Carbon Samples

period during which mechanical erosion of the aerodynamic surface is occurring, which results in a composite curve combining the rate of chemical reaction and the rate of mechanical erosion. The reproducibility of the slopes for the constant rate portion of the curves is within $\pm 2.5\%$ for both types of carbon studied.

If the over-all reaction rate is given by the expression

$$R = k(\text{CO}_2)(C)$$

where k is the specific reaction constant and is equal to $Ae^{-E/RT}$, (CO_2) is the average concentration of the carbon dioxide flowing along the exterior of the sample, and (C) is the concentration of the carbon expressed in terms of carbon reacting, it is seen that for negligible amounts of carbon monoxide formed and assuming the concentration of carbon a constant, as is usually done, the over-all reaction rate is essentially proportional to the specific reaction rate constant. The Arrhenius equation can then be used directly by plotting reaction rate in weight loss per unit time versus the reciprocal of the absolute temperature, as is shown in Figure 4. These plots indicate an apparent activation energy of 48 kcal. per mole for the graphite over the temperature range 900° to 1200° C. and 47 kcal per mole for the gas-baked carbon over the temperature range 900° to 1100° C. It is evident in the case of graphite that there is a transition region in the vicinity of 1200° C. where the apparent activation energy undergoes a large decrease to 26 kcal. per mole and mass transfer becomes a contributing resistance.

Surface Area Development during Reaction. To determine changes in surface area of the carbon samples resulting from reaction with carbon dioxide, the low temperature adsorption of carbon dioxide was measured, and the results were characterized by the well-known relationship developed by Brunauer, Emmett

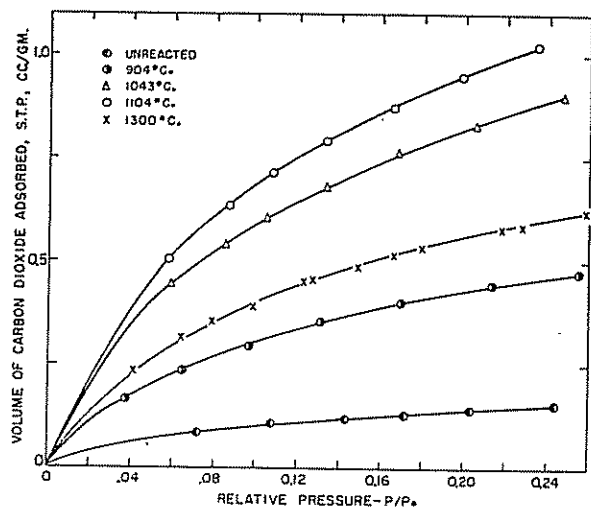


Figure 5. Adsorption Isotherms of Carbon Dioxide at 194.6° K. on Gas-Baked Carbon Reacted at Different Temperatures—One Gram Reacted

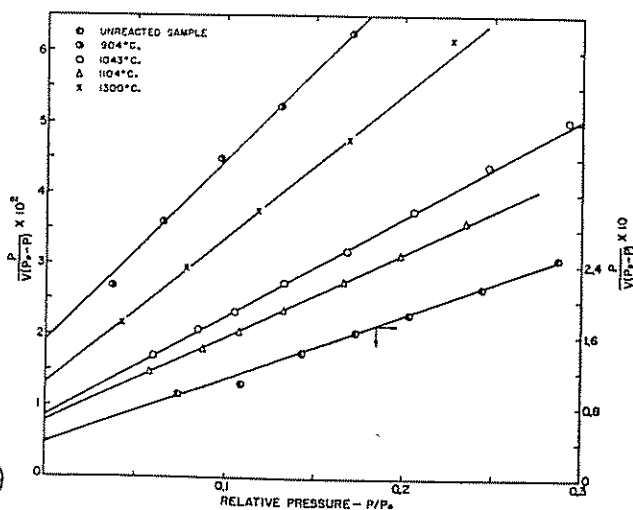


Figure 6. Simple B.E.T. Plots for Adsorption of Carbon Dioxide on Gas-Baked Carbon Rods with One Gram Reacted at Different Temperatures

Table III. Changes in Surface Area per Unit Length of Carbon Rods with Reaction Time

Reaction Time, Min.	Instantaneous Reaction Rate, G./Hr.	Weight Loss, G.	Area, Sq. M./Cm.	
			Gas-Baked Carbon	Graphite
0	0.71	0	1.2	
10	1.43	0.18	2.7	
20	2.16	0.48	4.8	
40	2.16	1.18	4.5	
Graphite				
0	0.86	0	1.1	
10	1.04	0.18	7.7	
20	1.76	0.41	14.6	
40	1.76	1.00	14.0	
67	1.76	1.77	14.1	

and Teller (5). The monolayer volume, V_m , determined in the usual way, was converted to a specific surface area by using the area of the carbon dioxide molecule in the liquid state of 17.0 square A. per molecule (4). Results for the variation in surface area per unit length of the carbon samples with reaction time are shown in Table III. The gas-baked carbon samples were reacted at 1050° C. and the graphite at 1100° C.

These results show that the internal surface area of both carbons increases rapidly during the early stages of the reaction during which time the reaction rates are also increasing. Unfortunately, accurate surface area data for the gas-baked carbon were not obtained for longer reaction periods due to the fact that the surface became extremely friable and difficulty was experienced due to handling losses during transfer to the B.E.T. apparatus. For the graphite rods, however, the surface was quite firm and accurate determinations of total surface area were possible for somewhat greater weight losses. The data indicate that B.E.T. area attains a maximum at substantially the same time that reaction rate becomes constant and remains essentially constant during the period of constant reaction rate.

Effect of Reaction Temperature and Type of Carbon on Surface Area Development. Rods of gas-baked carbon and graphite were reacted to a weight loss of 1 gram, or approximately 10%. These carbon samples were then studied by the low temperature adsorption of nitrogen, argon, and carbon dioxide. Figures 5 and 6 show, respectively, the adsorption isotherms and B.E.T. plots for carbon dioxide on all the gas-baked carbon samples reacted. Figures 7 and 8 show similar adsorption data for argon. Comparable adsorption isotherms of carbon dioxide on graphite were obtained and were similar in shape to those shown for the

Table IV. Surface Areas Produced for Graphite Rods at Different Temperatures—One Gram Reacted

Reaction Conditions, °C.	V_m , Cc.	Total Area, Sq. M.	Surface Area ^a , Sq. M./G.
Nitrogen			
Unreacted	2.1	9.3	1.0
904	7.6	33.3	3.9
1043	13.5	59.2	7.1
1104	16.4	71.8	8.5
1300	7.8	34.2	4.1
Carbon Dioxide			
Unreacted	1.1	5.4	0.6
904	5.6	25.7	3.0
1043	10.3	47.2	5.7
1104	13.2	60.2	7.2
1300	6.5	30.0	3.6
Argon			
1300	9.0	35.8	4.3
1300 ^b	9.3	35.2	4.2

^a This surface area is not a specific surface area in the true sense since the reacted carbon samples are no longer homogeneous.
^b Determined in liquid air, 80.6° K.

gas-baked carbon. Likewise, the adsorption isotherms for nitrogen on both carbons were similar to those shown for argon.

From the B.E.T. plots, for the majority of the samples, there is no difficulty in determining the slope of the lines over the usual relative pressure limits. To determine the surface area of the carbon samples from adsorption data at -196°C ., a molecular area of 16.2 square A. was employed for nitrogen (4) and 13.8 square A. for argon. The latter is based on the value of 14.4 square A. at -183°C . (4) corrected for the change in density of

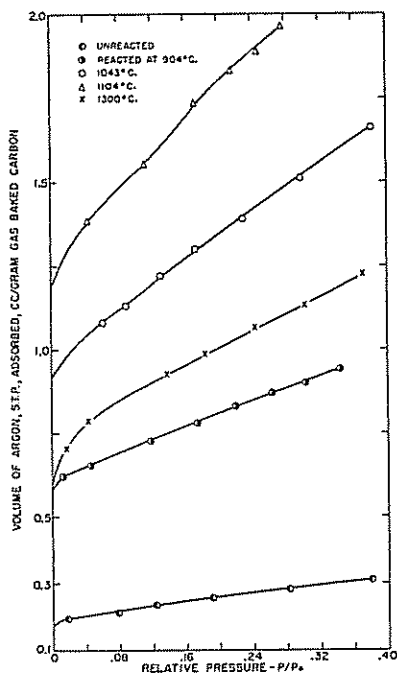


Figure 7. Adsorption Isotherms of Argon at 77.1°K . on Gas-Baked Carbon Rods Reacted at Different Temperatures—One Gram Reacted

liquid argon with temperature, assuming that the area varies inversely as the $2/3$ power of the liquid density. As previously stated, an area of 17.0 square A. is used for carbon dioxide. Table IV presents the surface areas of the graphite samples as determined by nitrogen, carbon dioxide, and argon adsorption. Table V shows similar data for the gas-baked carbon rods. Table VI gives the ratio of the surface area of graphite to that of gas-baked carbon at different temperatures as determined by the three gases.

These surface area data show that with the exception of the gas-baked carbon sample reacted at 904°C ., the smaller the adsorbate gas molecule, the larger the reported surface area of the carbon sample. This is indicative of an appreciable number of pores in the carbon samples of diameters comparable to the molecular diameters of the gas molecules. It will also be noted that for all adsorbates the total surface areas for the graphite samples are appreciably larger than the total surface areas of the gas-baked carbon samples reacted at the same temperature and that different surface areas are produced at different reaction temperatures for the same weight of carbon reacted, with the areas increasing from the unreacted sample up to a reaction temperature of about 1100°C . and then decreasing at 1300°C .

Using the surface area data for carbon dioxide, reaction rates were calculated on a gram per hour per square meter of surface basis. The results are shown in Table VII.

The ratio of reaction rates of the gas-baked carbon to the graphite, when expressed on the carbon dioxide B.E.T. area

Table V. Surface Areas Produced for Gas-Baked Carbon Rods at Different Temperatures—One Gram Reacted

Reaction Conditions, $^{\circ}\text{C}$.	V_m , Cc.	Total Area, Sq. M.	Surface Area, Sq. M./G.
Nitrogen			
Unreacted	1.5	6.7	0.7
904	4.9	21.6	2.6
1043	7.5	32.7	3.9
1104	9.5	41.7	5.0
1300	5.3	23.2	2.8
Carbon Dioxide			
Unreacted	1.3	5.9	0.6
904	3.7	16.7	2.0
1043	6.7	30.5	3.7
1104	7.9	36.0	4.3
1300	4.7	21.0	2.5
Argon			
Unreacted	2.0	7.4	0.8
904	5.3	19.6	2.4
1043	8.9	33.3	4.0
1104	11.9	44.4	5.4
1300	6.6	24.6	3.0

Table VI. Ratio of Total Surface Area of Graphite to Total Surface Area of Gas-Baked Carbon Rods after Reacting One Gram

Reaction Conditions, $^{\circ}\text{C}$.	CO_2	Adsorbate N_2	A
Unreacted	0.9	1.4	...
904	1.5	1.5	...
1043	1.6	1.8	...
1104	1.7	1.7	...
1300	1.4	1.5	1.5

basis, are shown in Table VIII. These ratios at three different temperatures are essentially constant. Even though more data should be obtained to completely settle the question, the implication is that the gas-baked carbon has about four times as much active area as graphite per unit of total area, over the temperature range indicated. Such constancy of specific reaction rates seems to parallel the very close apparent energies of activation of the two carbons for the carbon dioxide reaction. That is, apparently the two carbons contain similar reacting sites; however, the number for the gas-baked carbon is greater. The greater number of active sites for the gas-baked carbon may be due to one or more of the physical differences between the carbons, such as crystallite size, crystallite orientation, quantity and/or type of ash. Current evidence does not warrant conclusions concerning the exact cause.

Change in External Dimensions of Carbon Samples with Reaction. It is evident from the substantial increase in surface area of the carbon samples, with reaction of only about 10% of the total sample weight, that some of the reaction is occurring beneath the surface or internally. Figure 9 brings out this fact even more strikingly, particularly for graphite. Rod A is a photograph of an unreacted graphite rod. As the size and appearance of the unreacted gas-baked carbon rod were identical, a picture of this sample is not included. The unreacted sample has a uniform diameter measurement of 12.65 mm. from top to bottom of the rod and weighs 9.48 grams. Rod B is an identical graphite sample from which 3.68 grams of carbon or 39% of the initial weight has been reacted at 1100°C . Although there is some pitting or roughening of the external surface, the sample still has a uniform diameter from top to bottom of 12.65 mm. Rod C is a gas-baked carbon sample, of original external dimensions identical to rod A, from which 3.79 grams or, again, about 39% has been reacted. The diameter of this sample is 11.45 mm. at the top and 10.00 mm. at the bottom. In the graphite sample, if exterior burning is defined as the decrease in the external dimensions of the rod, there was no such burning. However, for the gas-baked carbon sample, the external dimensions decreased

markedly, resulting in a 35% decrease in volume. Therefore, we may conclude that the graphite or slower reacting carbon undergoes much more internal reaction than does the gas-baked carbon. This was true for all samples investigated. Another direct observation supporting this fact is the ease with which a graphite sample, after being approximately half reacted, breaks into two parts. This apparently is a direct consequence of porosity developed throughout the sample. However, the gas-baked carbon, for the same weight reacted, fails to break easily and appears to leave a hard, unreacted inner core. From the appearance of the gas-baked carbon sample, much more of the reaction occurs at the base of the sample, where pure carbon dioxide is entering than at the top where there is some slight contamination with carbon monoxide. Since less than 0.1% of the carbon dioxide volume reacted, an idea of the powerful inhibiting effect of carbon monoxide is obtained. Undoubtedly the inhibiting effect occurred also in the reaction of graphite rods but is not evident in sample B because the reaction is occurring under the surface.

Further qualitative examination of these reacted carbon samples were made by peeling layers from the rod with a knife. In

Table VII. Specific Reaction Rates of Carbon Rods at Different Temperatures after One Gram Has Reacted

Reaction Temp., °C.	Reaction Rate, G./Hr.	Total Surface Area, Sq. M.	Specific Reaction Rate, G./(Hr.)(Sq. M.) × 10 ³
Gas Baked Carbon			
904	0.25	16.7	14.9
1043	1.94	30.5	63.5
1104	4.08	36.0	113.4
1300	Too rapid
Graphite			
904	0.097	25.7	3.8
1043	0.74	47.2	15.7
1104	1.78	60.2	29.6
1300	9.09	30.0	300.3

Table VIII. Ratio of Specific Reaction Rates of Gas-Baked Carbon to Graphite Rods

Temp., °C.	Ratio
904	3.9
1043	4.0
1104	3.8

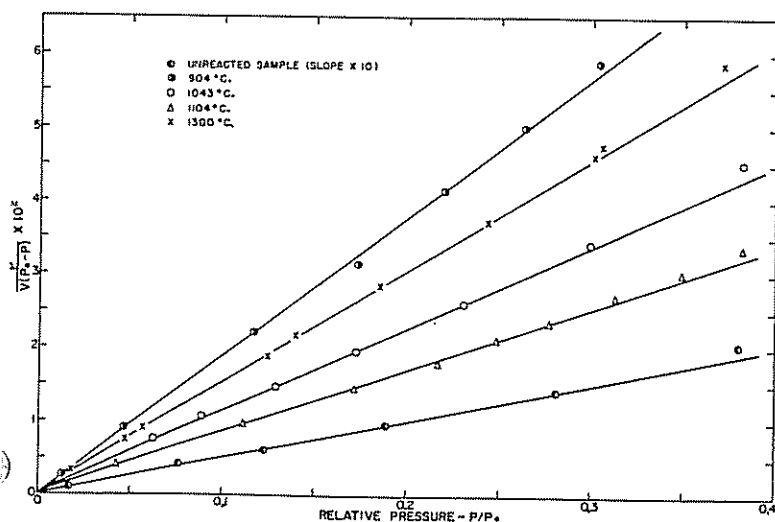


Figure 3. Simple B.E.T. Plots for Adsorption of Argon on Gas-Baked Carbon Rods with One Gram Reacted at Different Temperatures

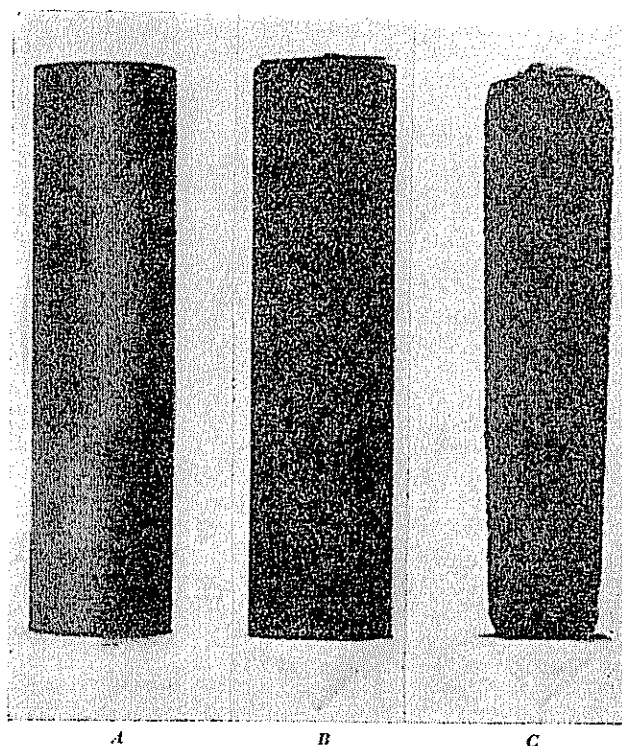


Figure 9. Change in Shape of Carbon Samples after Reaction

A = unreacted graphite; B = graphite, and C = gas-baked carbon, both reacted to 39% weight loss at 1100° C.

graphite there was a considerable depth which peeled away as easily as soft cheese. However, a point was reached where the hardness of the rod increased considerably and approximated that of the original graphite. For the gas-baked carbon, the exterior section could be scraped from the rod much more easily than on the original sample, but it lacked the softness and the depth of the graphite shell. Again, a hard inner shell, which appeared to be essentially unreacted, remained.

DISCUSSION OF RESULTS

The gasification of gas-baked and graphitized carbon with carbon dioxide over the temperature range, 900° to 1300° C., results in the following observations:

1. At constant temperature, B.E.T. area increases during the initial stages of reaction and becomes essentially constant during a period of constant reaction rate; B.E.T. area is lower for gas-baked carbon than for graphite rods over all stages of gasification herein investigated; and reaction rate per unit B.E.T. area is about four times greater for gas-baked carbon than for graphite rods up to a temperature of at least 1100° C.

2. For the same carbon, B.E.T. area increases up to a temperature of about 1200° C. and then decreases; reaction rate per unit area increases with increase in temperature over the entire range investigated; the apparent activation energy is 47 kcal. per mole for gas-baked carbon over the temperature range 900° to 1100° C., and 48 kcal. per mole for the graphite over the temperature range 900° to 1200° C.; the apparent activation energy of graphite between 1200° and 1400° C. is 26 kcal. per mole.

3. B.E.T. area for both reacted and unreacted carbon rods was found to increase with decreasing size of the adsorbate molecules.

These observations lead added insight into

roth the gasification mechanism of the carbon-carbon dioxide reaction and also the nature of the carbon rods reacted.

The decrease in adsorption volume and B.E.T. area with increasing size of adsorbate molecule is consistent with the idea that a fraction of the surface area of the carbon rods is reached through such small capillaries as to exclude carbon dioxide but admit argon molecules. Furthermore, the relatively high porosities (24.4 and 26.0%) of the 200-mesh carbons in powdered form contrasted with the relatively low areas of the unreacted graphite and gas-baked carbon rods which were made from this powder appear to imply not only the existence of small capillaries but also the presence of many unconnected capillaries. These conclusions are in line with the findings of Mantell (12), who reports that although the porosities of most carbon and graphite products range from 18 to 32%, such porosities are generally not a usable function as the pores are irregular in shape and for the most part unconnected.

The gasification mechanism as interpreted from the surface area results appears to be as follows: During the initial stages of reaction, the reactant gas diffuses into the interconnected capillary structure of the carbon and combines with exposed carbon active sites. Reaction develops new surface by enlarging to some extent existing macropores but principally by opening up pore volume not previously available to the reactant gas because the microcapillaries were too small or because existing pores were unconnected. The latter should be many times more effective at opening up new area (which for the most part is always in existence but inaccessible) than simple reaction of previously accessible area. During this stage, reaction rate will be controlled by the concentration of available reaction sites with the rate increasing steadily with increase in surface area. After the maximum surface has been developed, at approximately 10% burnoff for the two rod carbons investigated, the surface area attains essentially a constant value, where the rate of formation of new area is paralleled by the rate of destruction of old area. In developing the internal surface, a porous reacting shell of definite thickness is formed, the volume of which remains essentially constant for a given carbon and temperature, but differs for carbons of different reactivity. Concurrent with the attainment of a constant surface area the reaction rate attains a constant value which represents a dynamic balance between internal diffusion and chemical reaction.

The surface area developed for a constant weight of carbon gasified is a function of the type of carbon and the gasification temperature, other conditions constant. The type of carbon reacted at a given temperature can affect the area developed both by differences in gasification and internal diffusion rate. Adequate data are available on the differences in gasification rate of the two carbons, but information on differences in the diffusion rates, if any, for carbon dioxide through the porous structure of the carbon rods is, at present, lacking. However, any difference in the size of the pores in the two carbons or the number of pore constrictions would affect the internal diffusion rate.

Increase in gasification temperature, of course, increases the reaction rate, the internal diffusion rate, and the mass transfer rate of gas to the aerodynamic surface. The areas developed for both carbons with 10% weight reacted increase with increase in temperature over the range 900° to 1100° C. This is also the region where chemical reaction is usually considered the important resistance. However, the areas at 1300° C. for both carbons decrease sharply from their maximum values at 1100° C. This suggests that the maximum area per unit weight loss is obtained at the point where transition from chemical to mass transfer control begins. For the graphite rods this point would appear to be at about 1200° C.

The larger the resistance of mass transfer to the aerodynamic surface becomes with respect to other resistances the more the reaction should occur close to or at the aerodynamic surface of the carbon rod. This implies that increasing control of the reaction by mass transfer should result in a smaller and smaller developed internal surface area with reaction. Although the surface area at 1300° C. was materially less for both carbons than at 1100° C., it is still appreciably greater than that for the unreacted rods. This fact and the 26 kcal. per mole activation energy for graphite, which is considerably greater than 2 to 3 kcal. per mole usually associated with mass transfer being the major resistance and considerably lower than that in the lower temperature region, suggests that at 1300° C. the mechanism is still well within the transition region.

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