

Kinetic Study of the Steam-Carbon Reaction

INFLUENCE OF TEMPERATURE, PARTIAL PRESSURE OF WATER VAPOR, AND NATURE OF CARBON ON GASIFICATION RATES

Factors that influence the rate of reaction between carbon and steam were studied with emphasis on effects of temperature, partial pressure of water vapor, and nature of the carbon.

Reactivities of seven samples of carbon rod were determined by two independent methods based on loss of weight of carbon with time, and composition and flow rate of the product gas. Reactivity of the carbons decreased as the degree of graphitization increased and as electrical resistivity decreased. From 1000° to 1100° C., the over-all energy of activation for reaction of a graphitized carbon was found to be 41 kcal. per mole. At 1100° C. from 30 to 360 mm. of mercury (water vapor), the apparent order of the reaction for a graphitized carbon with respect to steam was 0.66.

The results of this research emphasize the important part played by the nature of the carbon in determining the rate of gasification of carbon with steam.

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IN ORDER to improve methods for the gasification of solid fuels, fundamental information is needed concerning the rate and mechanism of the steam-carbon reactions. The literature contains a number of papers (1, 5-7, 9, 10, 12, 13, 15, 21, 22) concerned with the kinetics of these reactions, but the reports by various investigators are in many respects contradictory and confusing. For example, the order of the reaction with respect to steam has been reported by different authors as negative,

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zero, fractional, first, second, or unknown. Gadsby, Hinshelwood, and Sykes (5) account for much of the disagreement on the basis that the retarding effect of hydrogen is often overlooked in determining the reaction order. A wide variation in the type of carbon studied, ranging from coal to graphite, undoubtedly also has had a major effect on the inconsistencies of the results.

Regarding the mechanism of the reaction, it has been shown rather conclusively in two recent papers, one by Long and Sykes (13) and one by Johnstone, Chen, and Scott (9), that the primary product of the reaction between carbon and steam is carbon

monoxide. The authors, as well as Goring and others (8), have shown that the gasification rate is strongly inhibited by hydrogen and not inhibited by carbon monoxide.

The purpose of the present work was to study the influence of temperature, partial pressure of water vapor, and nature of carbon on the rate of the steam-carbon reactions. Most of the prior publications on this reaction have failed to give a definitive description of the carbon samples used. In general, samples were described only by such terms as "charcoal," "coke," "carbon electrodes," and "graphite electrodes"—descriptions that have little meaning unless additional information on physical properties and the previous history of the carbons is included. For each experiment of this investigation, a carbon or graphite rod of known physical properties was used, and the rate of reaction with steam was calculated by two independent methods based either on the rate of weight loss experienced by the sample or on the composition and flow rate of the effluent gases.

APPARATUS

Figure 1 is a flow sheet of the apparatus, which consisted of equipment for reaction of the carbon specimen with steam, with close control of temperature, partial pressure of water vapor, and rate of gas flow. Nitrogen gas was purified by passage through an anhydrous magnesium perchlorate drying tube to remove traces of water vapor and by passage over copper gauze heated to 800° C. to remove traces of oxygen. A rotameter indicated the flow rate of the dry nitrogen.

Figure 2 shows the saturator (designed and built by R. D. Hinkel) in which the dry nitrogen was saturated with water vapor. (During the preliminary heating of the carbon prior to reaction, the dry nitrogen was allowed to bypass the saturator.) The water level in the saturator was maintained constant by means of the side-arm device shown at the left of Figure 2.

When the water level dropped below the sloped opening to the 10-mm. tubing, a bubble of nitrogen passed up into the water-jacketed buret and allowed an equal volume of water to enter the saturator. The saturator operated well and made it possible to measure the amount of water vaporized with an accuracy within about 2%.

Test runs made over a wide range of saturation temperatures showed that the gas was 95% saturated with water vapor. The saturator unit was immersed in a water bath heated by two 750-watt copper-sheathed flexible-type immersion heaters each 4 feet long. A stirrer 3 inches in diameter provided ample agitation throughout the bath.

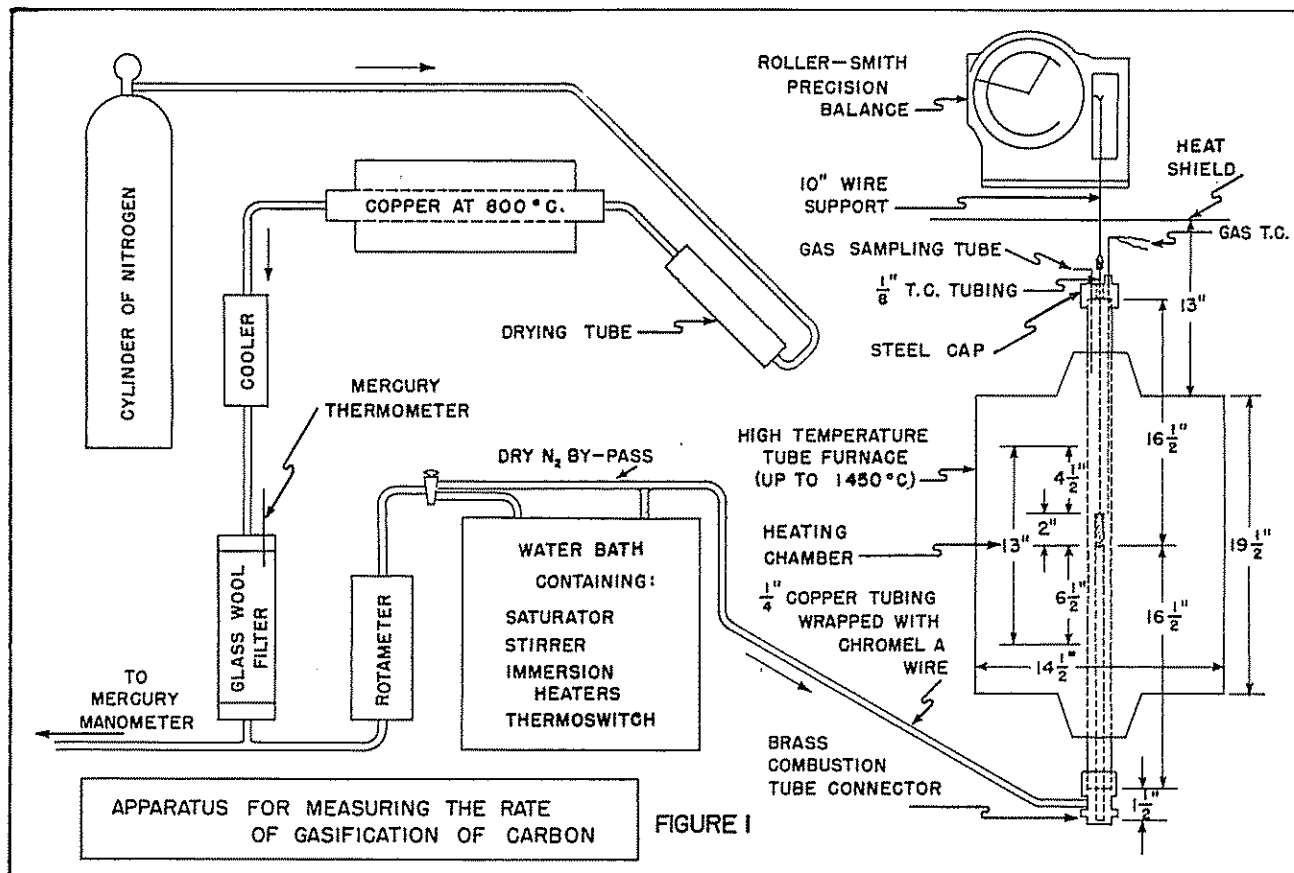
To make sure that no condensation of water vapor took place while the gas was flowing through the tubing from the saturator to the reactor, the outside tube wall was wound with Chromel resistance wire and maintained at a temperature slightly above 100° C.

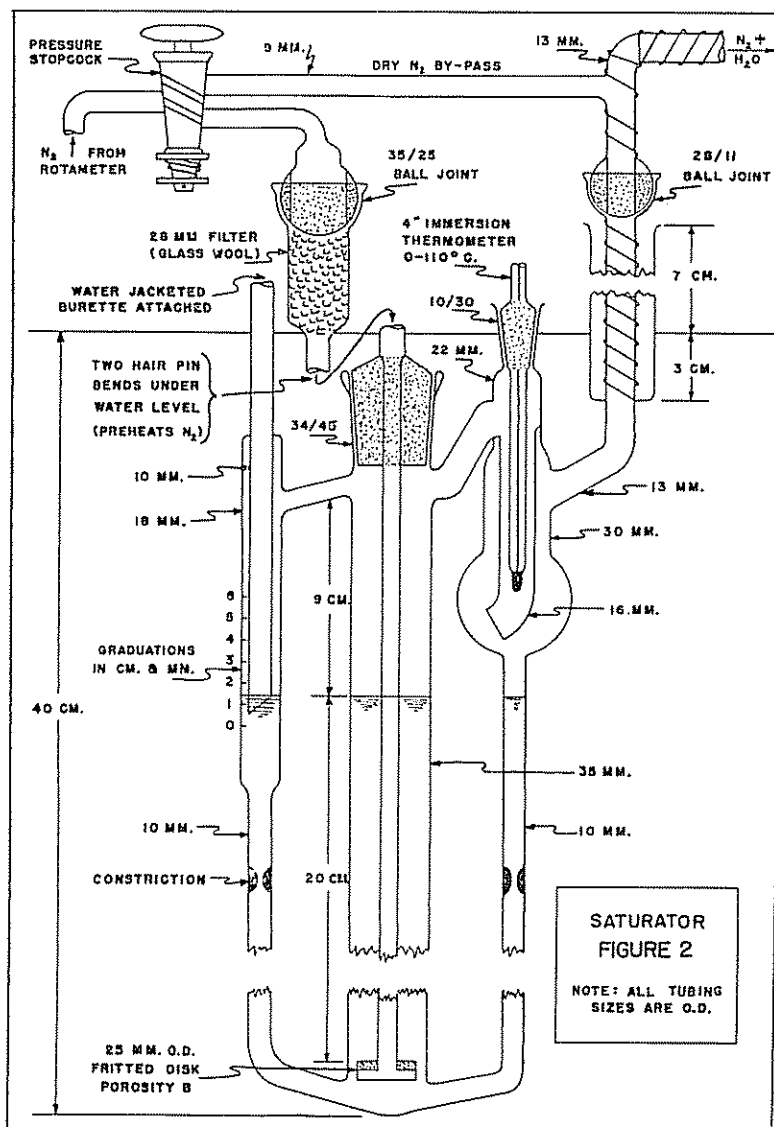
Figure 3 is a detailed section drawing of the reactor ready for a test. The reactor was essentially the same as that described fully in recent studies of the carbon-carbon dioxide reaction (19).

NATURE OF CARBON USED

... is an overlooked factor in steam-carbon reactions

Studies presented here will aid in improving processes for gasifying solid fuels





Briefly, a porcelain "top plate" and "bottom cone" were cemented to the top and bottom, respectively, of the carbon rod to restrict reaction to its sides. The sample was suspended from a balance so that frequent weight readings could be taken during the run. (It was not necessary to interrupt the gas flow when reading the weight of the sample, because the gas velocity was so low that weight readings were not measurably affected.) A platinum-platinum-10% rhodium thermocouple, with hot junction located at a point level with the top of the sample, indicated reaction temperature, which could be maintained within 2° C. of the desired value. (Preliminary tests at 1100° C. showed that a thermocouple located in the center of the carbon sample indicated the same temperature within 2° C. as the thermocouple placed in the gas stream.) The effluent gases were sampled through a tube passing through the steel cap located on top of the porcelain combustion tube.

CARBON SAMPLES

Seven different samples of carbon (supplied through the courtesy of H. W. Abbott and G. P. McKnight, Speer Carbon Co.) were used in the investigation. Table I summarizes the properties of these artificial carbons and graphites. Sample A was used for all test runs made to determine the influence of temperature and partial pressure of water vapor on rate of reac-

tion, and all seven samples were tested under similar conditions to determine the influence of the nature of the carbon on reaction rates. All the samples except G were made by extruding a mixture of about 70% petroleum coke flour (60% through 200-mesh) and 30% coal-tar pitch binder and heating to the appropriate temperature. Sample G was a special graphitized carbon prepared by substituting anthracite for the petroleum coke. The test specimen consisted of a solid rod of carbon, 0.5 inch in diameter and 2 inches long.

PROCEDURE

The test procedure consisted essentially of determining reaction rates by taking weight readings of the carbon sample at 5- to 15-minute intervals, while providing accurate control of temperature, partial pressure of water vapor, and rate of gas flow. The three variables studied were: temperature over the range 1000° to 1450° C., partial pressure of water vapor over the range 30 to 360 mm. of mercury, and nature of the carbon, particularly the degree of crystallinity or graphitization, as determined by x-ray diffraction.

The total rate of gas flow (nitrogen plus water vapor) was 1250 cc. per minute, measured at 70° F. and 760 mm. of mercury pressure. The flow past the carbon rod was laminar, as the Reynolds number was always under 20. The contact time between the steam and the carbon rod was about 0.25 second.

Reaction rates were also determined by analyzing samples of the product gas with a Burrell laboratory model apparatus. Samples were obtained by drawing the gas directly into the water-jacketed buret at a rate approximating one-tenth of the total gas-flow rate. The sampling tube and manifold had previously been flushed with gas. The sample was collected after about 25 to 30% weight loss of the specimen had occurred, at which time the rate of reaction was found to be very uniform.

RESULTS AND DISCUSSION

Typical Run. Figure 4 shows how the weight-loss data were plotted against reaction time to obtain a reaction rate curve. The rate of reaction for this particular run was practically constant for the first hour, during which time the sample lost 4 grams, or 40% of its original weight. Test runs were usually stopped at this stage of reaction, but this run was continued until the sample was completely consumed as indicated by the fact that no further loss of weight occurred. The rate of reaction on the straight part of the curve was 4.03 grams per hour based on

Table I. Description of Carbons and Graphites

Sample	Treatment ^a	Apparent Density, G./Cc.	Resistivity, Ohm/Inch Cube	% Ash ^b
A	Graphitized twice at approx. 2500° C.	1.57	0.00037	0.07
B	Gas baked at 935° C.	1.55	0.00130	0.45
C	Superbaked at 1095° C.	1.56	0.00115	0.75
D	Graphitized once at approx. 2500° C.	1.58	0.00041	0.09
E	Graphitized twice at approx. 2500° C.	1.57	0.00039	0.10
F	Graphitized thrice at approx. 2500° C.	1.56	0.00038	0.16
G	Graphitized once at approx. 2500° C.	1.72	0.00064	0.37

^a Samples B, C, D, E, and F were all prepared from the same batch of raw material but given different treatments as indicated. Sample A was prepared from a separate batch, but given same treatment as E.

^b Ash from gas-baked carbon B was very dark in color, ash from superbaked carbon C was medium brown, and ash from graphitized carbons was very light tan or light gray.

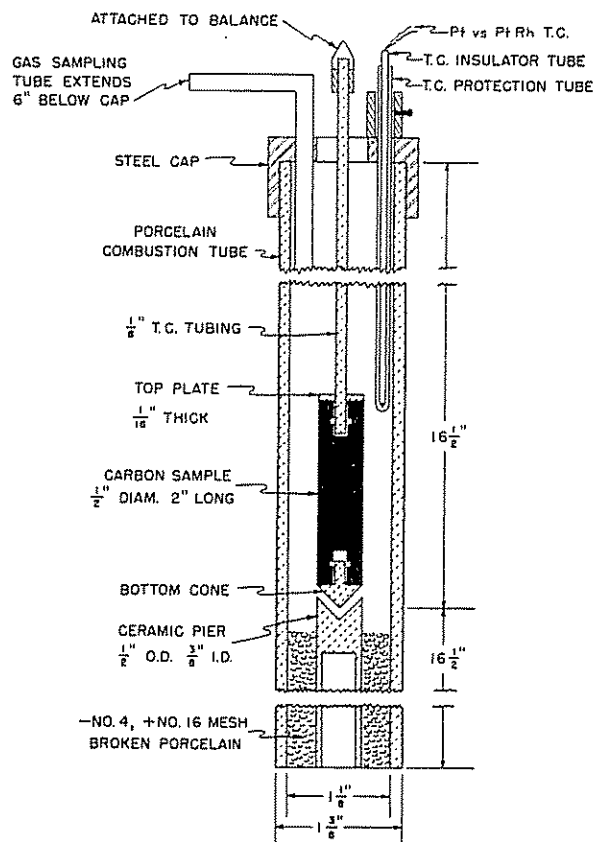


Figure 3. Section drawing of carbon sample in combustion tube

weight-loss data and 4.10 grams per hour based on gas-analysis data. The accuracy of weight measurements was considerably better than the accuracy of gas analyses, so the rates determined from weight data were used for the kinetic calculations.

The general shape of the weight-loss time curves was similar to those previously reported for the carbon-carbon dioxide reaction (19). At temperatures below 1100° C., an initial induction period, during which the gasification rate increased with time, was in evidence, whereas, at higher temperatures, no induction period was detectable on the time scale employed. For the carbon-carbon dioxide reaction, it was shown that the induction period could be directly related to increasing surface area of the sample. With the attainment of constancy of surface area, the reaction rate became constant. The same general pattern is expected to be followed by the steam-carbon reaction. An induction period is to be expected for reaction temperatures above 1100° C., as well as at the lower temperatures; however, its duration should be short for two reasons. First, as shown by Walker, Foresti, and Wright (19) and more recently by Petersen, Walker, and Wright (16), for the carbon-carbon dioxide reaction, the maximum equilibrium surface area is attained at a temperature of roughly 1200° C.; and second, because reaction rate increases rapidly with temperature, less time is required to achieve the weight loss necessary to produce the equilibrium surface area. If similar reasoning can be used for the present steam-carbon reaction (and there is every reason to believe it can), there would be some temperature, apparently again around 1200° C., where the induction period is of the order of several minutes, or less, in duration.

Reproducibility of Test Method. In order to determine the reproducibility of this test method, six duplicate runs were made on sample A at 1100° C. The highest reaction rate observed on the straight portion of the curve was 1.35 grams per hour; the lowest was 1.25 grams per hour. The rate was determined after

the sample was about 25% reacted, at which time the rate of reaction was substantially constant.

Influence of Temperature. The first complete series of runs was made on sample A at temperatures varying from 1000° to 1450° C., while the inlet partial pressure of water vapor was maintained essentially constant at 142 mm. of mercury.

Figures 5 and 6 present the reaction rate curves. Figure 7 shows the samples as they appeared immediately after testing, and again as they appeared after removal of the porous layer that had formed. The upper pictures show that the specimens reacted at 1050° and 1100° C. experienced no change in external dimensions, which indicates that the reaction was highly "selective" in nature—that is, the more reactive particles of carbon were removed by gasification with steam and the less reactive carbon particles remained in place as a fragile, porous layer, which could easily be removed by scraping with a knife blade. Similar results have been reported by Walker, Foresti, and Wright (19) for the carbon-carbon dioxide reaction. The specimen reacting at 1200° C. showed a slight reduction in diameter near the bottom, and, as the temperature of reaction was increased, the decrease in diameter was more pronounced.

The weights of the porous layers removed from the specimens are tabulated at the bottom of Figure 7. Those specimens reacting at the two highest temperatures had almost no porous layer, which shows that the reaction at the higher temperatures was much less selective than at lower temperatures. This porous layer is believed to be responsible for the majority of the increase in surface area of a carbon. Therefore, the maximum surface area would be expected between 1050° and 1100° C., in the present case. Thus, as previously reasoned, the time for the development of this layer, even disregarding for the moment increase in reaction rate, should be less at temperatures above 1100° C., resulting in the attainment of a constant reaction rate more quickly at the higher temperatures.

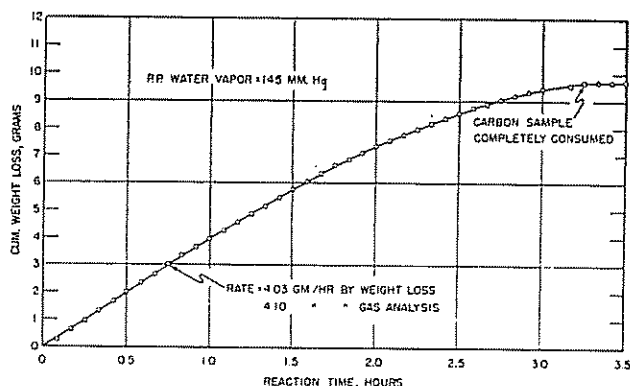


Figure 4. Reaction rate curve for sample A completely gasified at 1300° C.

The rate of reaction was more rapid near the bottom of a sample than near the top, especially at the higher temperatures. This was attributed to two factors: The steam was being decomposed so rapidly that the partial pressure of water vapor was greater toward the bottom of the specimen, and hydrogen was being formed as a product and tended to retard the rate of reaction of the upper portion of the sample.

Activation Energy. Figure 8 shows the Arrhenius plot from which the energy of activation was calculated for sample A. In making this plot, it was assumed that the over-all reaction rate is given by the expression

$$R = k(\text{H}_2\text{O})^n(\text{C})^m$$

where k is the specific reaction constant, (H_2O) is the average concentration of the water vapor flowing along the exterior of the

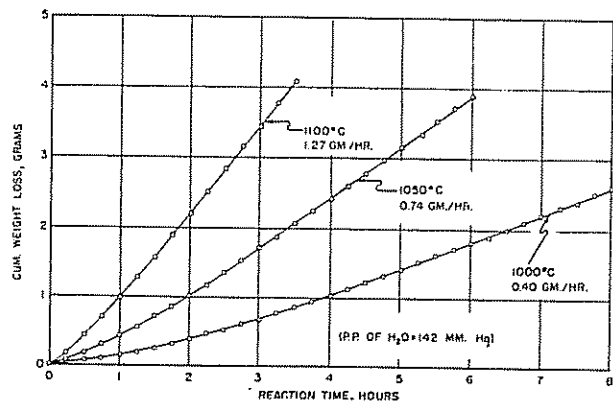


Figure 5. Reaction rate curves for sample A at various low temperatures

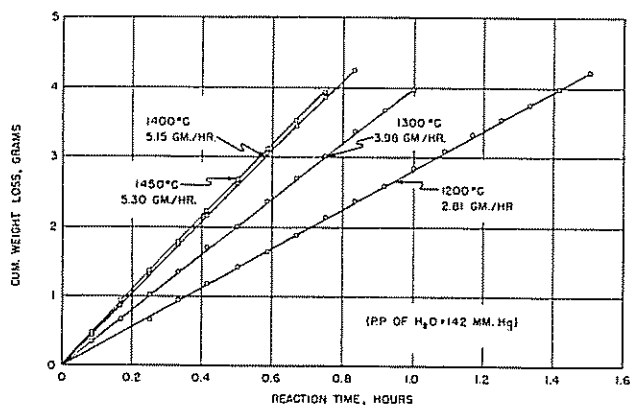


Figure 6. Reaction rate curves for sample A at various high temperatures

sample, and (C) is the concentration of the carbon reacting. It was then assumed that the concentrations of water vapor and carbon were constants, independent of temperature. As long as experimental conditions were such that these assumptions were valid, the Arrhenius equation could be used directly by plotting log of reaction rate, expressed as weight loss per unit time, against the reciprocal of the absolute temperature. Figure 8 shows that the above-stipulated conditions appeared to be relatively well satisfied over the temperature range 1000° to 1100° C., giving an activation energy of 40.7 kcal. per mole. Mayers (15), working with a graphite, found the energy of activation to be 49.7 kcal. per mole over the temperature range 850° to 1000° C. and 35.1 kcal. per mole over the range 1000° to 1160° C. Fleer and White (3), working with coke, reported a value of 26.8 kcal. per mole for the temperature range 900° to 1000° C.

The decrease in activation energy for the reaction above 1100° C. is attributed to two main causes. At temperatures above 1100° C., the partial pressure of the products along the exterior of the sample becomes significant, invalidating the assumption that the water vapor concentration is a constant, independent of temperature. Secondly, resistance of mass transport of the steam to the carbon active sites is known to become a significant factor at higher temperatures and to have a lower activation energy than the chemical resistance term (23).

Influence of Partial Pressure of Water Vapor. In order to determine the influence of partial pressure of water vapor on reaction rate and to obtain data for calculating the apparent order of reaction with respect to steam, runs were made with sample A, employing a partial pressure of water ranging from 30.7 to 358 mm. of mercury at a constant reaction temperature of 1100° C. The rate of reaction, over the constant-rate portion of the runs, increased from 0.44 gram per hour at 30.7 mm. water-vapor pressure to 2.23 grams per hour at 358 mm.

Figure 9 is a plot of the data showing that a straight line is obtained giving an apparent order of reaction of 0.66, under the conditions specified. The term "apparent order of reaction" is used to refer to the experimentally determined value of n in the rate equation, $R = aP^n$, where R is the rate of reaction in grams per hour, a is an empirical constant depending upon the experimental method, and P is the partial pressure of water vapor in millimeters of mercury. The equation is identical to the classic Freundlich equation (4) for predicting the adsorption of gases on solids at intermediate pressures, a fact that again indicates (9) the close connection between chemisorption of the reaction gas on the carbon surface and the actual gasification of the carbon. Zeldowitch (24) points out that the Freundlich isotherm describes the chemisorption process if the active sites are distributed exponentially with respect to the energy of adsorption. Apparently, agreement with the Freundlich equation in the present case also implies the above. The fact that the apparent order of the reaction with respect to steam did not change noticeably over this pressure range indicates that the steam saturation pressure discussed by Warner (21, 22) was not closely approached.

Influence of Nature of Carbon. Most investigators agree that the reactivity of carbonaceous fuels is strongly influenced by degree of graphitization (14). In order to determine the influence of the nature of the carbon, expressed in terms of graphitization or "crystallinity," tests were made on all seven samples of carbon with the reaction temperature at 1100° C., the partial pressure of water vapor at 142 mm. of mercury, and the gas-flow rate at 1250 cc. per minute. The crystallinity of the carbons was determined by x-ray diffraction techniques, using the intensity of the (002) diffraction peak of the carbon, as previously discussed by Day, Walker, and Wright (2).

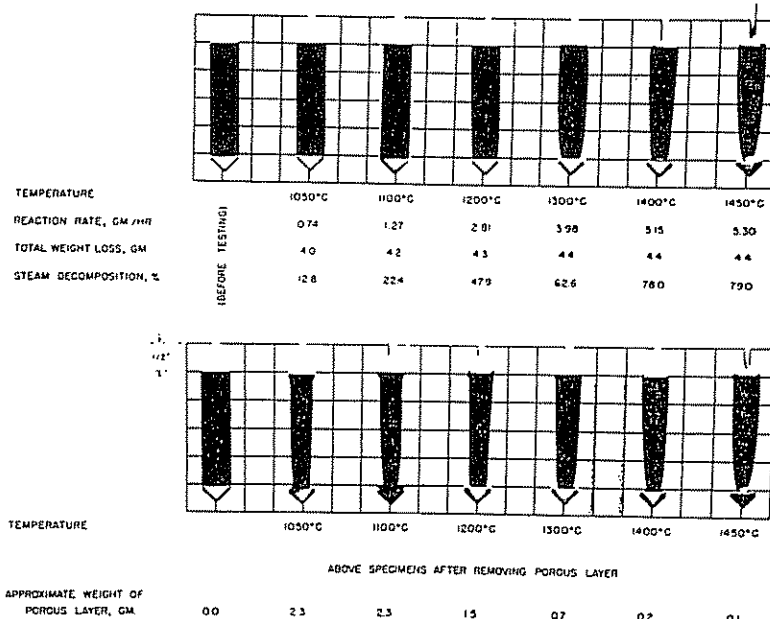


Figure 7. Specificity of reaction of sample A graphite with steam as a function of temperature

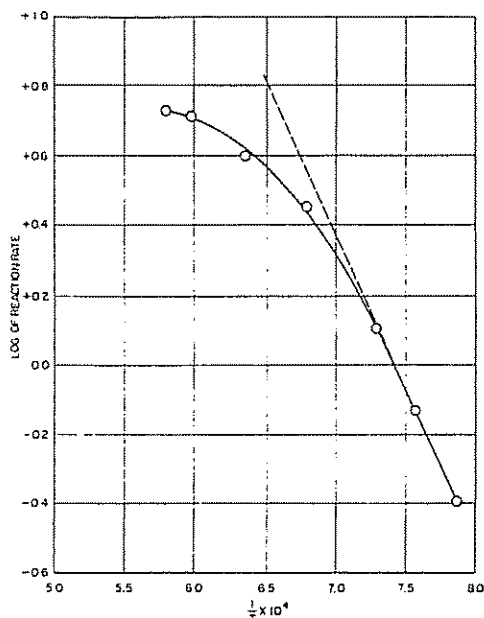


Figure 8. Arrhenius plot for sample A reacted with water vapor at 142 mm. of mercury pressure

Table II shows the correlation obtained between reaction rate and crystallinity. The second line of the table shows that the crystallinity of the porous layer scraped from sample A, after reaction at 1100° C., was 19% greater than that of the unreacted material. The increase is attributed to selective reaction, which removed the more reactive carbon and left in place the less reactive (more crystalline) material. This is similar to the findings of Walker, McKinstry, and Pustinger (20), who examined graphitized carbon rods by x-ray diffraction after varying degrees of gasification with carbon dioxide.

The results obtained on samples B, C, D, E, and F, all of which were prepared from the same batch of raw material, indicate that reactivity decreases as crystallinity increases and that graphitization for a second and third time at the same temperature has no appreciable influence on reactivity or on crystallinity. Apparently the temperature of graphitization is the important factor, and time, beyond the first period of graphitization, is unimportant. This is in agreement with the findings of Schaeffer, Smith, and Polley (17), who report from rough rate measurements that equilibrium growth during graphitization of carbon blacks at temperatures around 2700° C. may be attained within a matter of 10 minutes. In the present case, during the first graphitization step, the carbon was held at the maximum graphitization temperature, of roughly 2500° C., for considerably longer than this period.

The result of the test on anthracite-base sample G indicates that other properties besides carbon crystallinity influence the

Table II. Correlation between Reaction Rate at 1100° C. and Crystallinity of Carbon Samples

Sample	Reaction Rate, G./Hr.	Crystallinity
A	1.27	100
A (porous outer layer after reaction)	..	119
B	2.18	39
C	1.7 ^a	70
D	1.59	100
E	1.64	97
F	1.63	96
G	1.84	84

^a Reaction rate for superbaked sample C tended to increase gradually as test proceeded; consequently, measurement of rate was less precise.

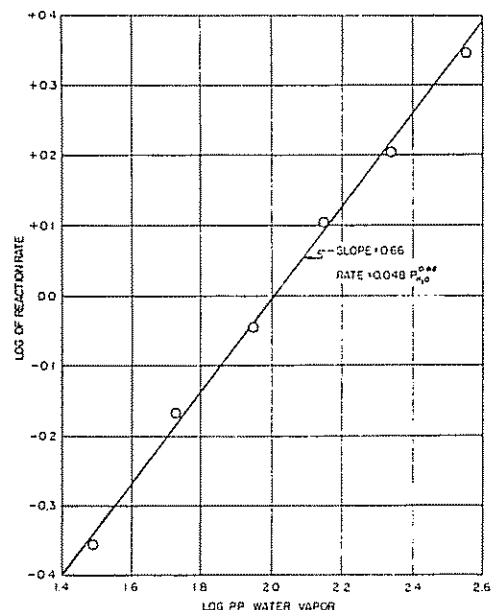


Figure 9. Apparent order of reaction for sample A at 1100° C.

reactivity of the steam-carbon reaction. Referring to Table II again, sample G is between the gas-baked and superbaked materials with respect to reactivity, but is between the superbaked and graphitized materials with respect to crystallinity. Reference to Table I shows that the graphitized anthracite is also intermediate between the superbaked and graphitized materials in so far as resistivity and per cent ash are concerned. The apparent density is considerably higher for the graphitized anthracite than for any of the other carbons and this may account for its higher reactivity. However, the high density of the graphitized anthracite implies a smaller pore volume which, if anything, should cause a decrease in reactivity owing to the smaller amount of interior surface available for reaction.

Further evidence that crystallinity of the carbons is not the only parameter affecting their reactivity is gained by comparing sample A with sample E. Both have been graphitized twice and both have essentially the same crystallinity, and yet sample A has a reactivity 30% lower than sample E. It is further seen that the resistivity and total ash content of samples A and E are the same, within experimental error, and would not be expected to explain the differences in reactivity. Further study of more carbons having a wider range of properties such as surface area, porosity, and pore size distribution is necessary before the differences in reactivities can be completely explained.

Per Cent Steam Decomposition. Table III presents the analyses of the product gas and the per cent steam decomposition for the various tests. The gas samples were collected after the carbon samples had lost about 25 to 30% of their weight, at which time the rate of reaction was substantially constant. From the analyses and the knowledge of the amount of water vapor in the inlet nitrogen, the amount of water vapor decomposed could be determined.

Figure 10 shows the effect of temperature on percentage steam decomposition for sample A. The amount of steam decomposed increased with increasing temperature continuously to 1450° C., the highest reaction temperature investigated. It is also seen from Table III that the percentage steam decomposition decreased with increase in the amount of entering steam. In essence, this is an outgrowth of the fact that the gasification rate varied with the steam partial pressure to some power less than one. Table III also shows that the percentage steam decomposition at 1100° C. and at a fixed steam inlet concentration is a function of the type of carbon gasified. The gas-baked carbon,

Table III. Analyses of Product Gas (Dry Basis) and Per Cent Steam Decomposition after Gasification under Different Conditions

Sample	Temp., ° C.	Partial Press. H ₂ O, Mm. Hg.	% CO ₂	% H ₂	% CO	% N ₂	% Steam Decomp.
Effect of Temperature							
A	1000	139	0.3	1.5	1.2	97.0	7.9
	1050	141	0.4	2.5	2.1	95.0	12.8
	1100	141	1.1	4.6	2.7	91.6	22.4
	1200	142	1.8	9.6	6.1	82.4	47.9
	1300	143	1.8	11.4	8.3	78.5	62.8
	1400	142	1.0	13.7	11.8	73.5	78.0
	1450	143	1.1	13.7	11.9	73.3	79.0
Effect of Partial Pressure of Steam							
A	1100	30.7	0.1	1.3	1.2	97.4	33.1
		53.5	0.3	2.4	1.4	95.0	26.6
		80.1	0.3	2.8	2.6	94.3	24.4
		210	1.1	0.2	4.4	88.3	17.4
		358	2.8	11.7	6.7	78.8	10.1
Effect of Carbon							
B C D E F G	1100	142	2.1	7.9	4.4	85.6	41.6
		142	1.2	5.6	3.8	89.4	28.6
		145	1.6	6.4	3.3	88.7	29.4
		144	2.1	6.8	3.0	88.1	32.7
		143	2.1	6.7	2.9	88.3	32.6
		142	1.0	7.3	3.1	87.7	32.4

B, gave the highest percentage steam decomposition. No significant differences were observed for the other carbons tested under the same conditions.

Equilibrium in Water-Gas Shift Reaction. The extent to which equilibrium was approached for the water-gas shift reaction was determined for sample A at various temperatures by calculating an "apparent equilibrium constant," K_{ap} , from the composition of the effluent gases by the relation

$$K_{ap} = \frac{(\% \text{ CO}_2)(\% \text{ H}_2)}{(\% \text{ CO})(\% \text{ H}_2\text{O})}$$

The K_{ap} was then compared with the true equilibrium constant reported by Wagman and others (18).

Figure 11 shows the ratio of K_{ap} to K_{eq} , as a function of temperature. At temperatures above 1300° C., the ratio is greater than one. As no special effort was made to quench the gas sample, this is probably due to reaction of the product gases as they pass

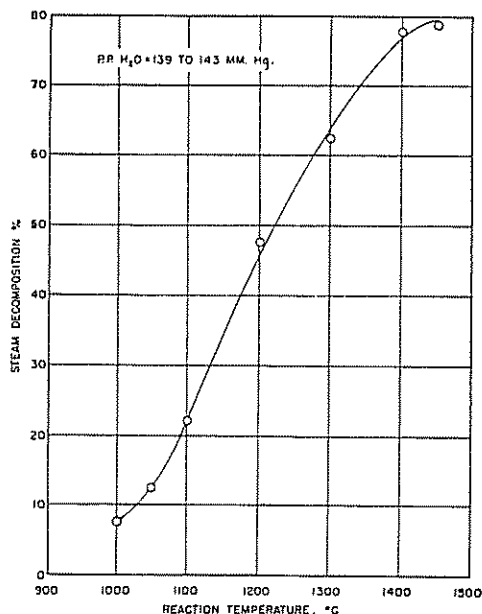


Figure 10. Effect of reaction temperature on per cent steam decomposition

the 2.25-inch distance from the carbon sample to the sampling tube. Therefore, since the equilibrium ratio is, if anything, higher than that opposite the graphite sample, this figure serves to show primarily that a temperature of at least 1300° C. is required to reach equilibrium conditions at the flow rate used.

Mechanism. The results of this research are in agreement with the generally accepted adsorption concept (11) used to explain the chemical mechanism of heterogeneous reactions in which the rate is determined by the concentration of gas adsorbed on the solid surface rather than by the pressure of the gas in the homogeneous phase.

A possible explanation of the physical mechanism that caused the porous layer to be formed on the surface of specimens tested at 1100° C. was gained from a study of electron micrographs of the unreacted sample A and of the porous layer. The micrographs of the unreacted graphitized carbon showed large cottonlike areas that appeared to consist of a number of thin platelike crystals in very disordered arrangement, whereas the material comprising the porous layer contained a high concentration of spherical shapes that tended to flocculate or collect in short chains and may have been oriented aggregates of platelike crystals which, because of their more ordered arrangement and reduced effective area, were apparently less reactive. The concentration of "active carbon centers" was probably less for the spherical shapes in the unreactive porous layer than for the cottonlike masses in the original graphitized carbon.

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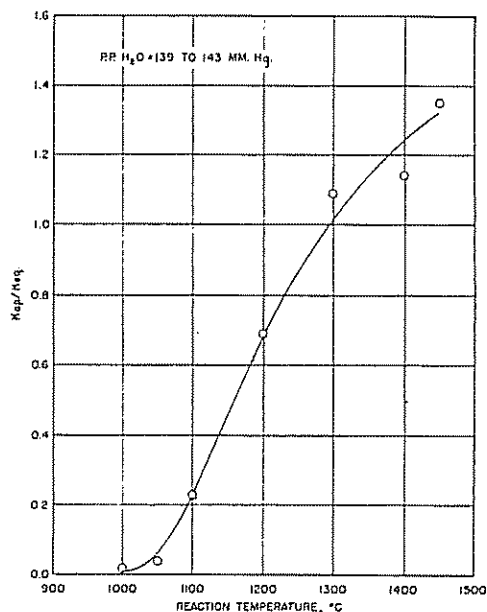


Figure 11. Effect of temperature on approach to equilibrium for water gas shift reaction

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