

rate at which samples react is largely controlled by chemical reactivity at the reaction site and steps 3 and/or 4 are controlling.

The bulk density profiles of graphite rods reacted at 1100° C. indicate that gasification occurs to a greater extent in the outer portions of the sample. The increase in temperature above 900° C. has increased the reactivity of the graphite more than the transport properties, so that the reactant can no longer be supplied with a negligibly small concentration gradient. Therefore, the concentration decreases with increasing depth of penetration and the reaction rate diminishes in the sample interior.

At 1300° C. diffusional effects become even more pronounced, and the reaction occurs predominantly in the outer portion of the sample. After the reactant has penetrated approximately 0.20 cm., the material at the external surface has been reduced to a bulk density of about 0.33 gram per cc. and at this point particles begin to fall from the sample. It is apparent that upon subsequent gasification, the rate at which the reactant penetrates

radially must become equal to the rate of decrease of outer sample radius; therefore, a reaction zone of constant thickness must result. The rate at which the integral reaction rate at 1300° C. decreases in Figure 11 is approximately proportional to the mean radius of the reaction zone. This suggests that the rate-decreasing period is due to a smaller volume of graphite undergoing reaction.

Utilizing the family of differential reaction rates obtained from data on bulk density profile, it is possible to calculate integral reaction rates of cylindrical samples at 1100° C. which agree closely with those actually measured at various reaction times. From these results, it would appear that there is little significance to the extended constant reaction rate zone at 1100° C. for the rod samples. A limited amount of data from plate samples at the same temperature indicates that the extended constant rate zone is not a general condition.

(Reaction of Artificial Graphite with Carbon Dioxide)

SURFACE AREA DEVELOPMENT WITHIN ARTIFICIAL GRAPHITE RODS REACTED WITH CARBON DIOXIDE FROM 900° TO 1300° C.

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SEVERAL investigators have noted that partial gasification of carbon results in an increase in the total surface area as determined by heat of wetting (4) and by low temperature gas sorption (9, 23). The rate at which a sample reacts at a given instant should be proportional to the total surface area, provided each unit area in that sample is reactive to the same extent and the reaction is not controlled by mass transport—i.e., diffusion and/or mass flow—of the reactant from the bulk gas phase to the reaction site and mass transport of the product from the reaction site to the bulk gas phase. Under these conditions, a reaction is chemically controlled—that is, the steps of activated adsorption, chemical reaction, and/or activated desorption are slow compared to the rates of mass transport of the reactant to and product from the reaction site, and therefore, only small concentration gradients are necessary to maintain the necessary transport rates so that the concentrations of reactant and product are essentially the same as in the bulk gas phase. On the other hand, if the reaction is diffusion controlled, there would probably not be a direct proportionality between total surface area and the rate at which a sample gasifies at a given reaction temperature.

Walker, Foresti, and Wright (23) have presented quantitative information on the total surface area developed within graphite rod samples when partially gasified at various temperatures. From their data, it is possible to compare Arrhenius plots on the basis of weight loss per unit time per unit area and of weight loss per unit time. This has been done in Figure 11. The magnitude of the activation energy decreases from about 48 to approximately 33 kcal. per mole (the plot based upon total surface area is not linear). It has been customary to express reaction rates of heterogeneous reactions in the form of Arrhenius plots without taking into account the total surface area, presumably because the magnitude of the total surface of the sample was not known. However, expressing the reaction rates on a per unit area basis decreases the magnitude of the activation energy and raises the question as to which basis is fundamentally more correct. The

partial answer to this question may be obtained, considering that the apparent activation energy of a first-order chemical reaction occurring in a uniform cylindrical pore in which diffusion and chemical reaction rates are simultaneously important is exactly one half the true activation energy of the chemical reaction, as is shown by Wheeler (25). The decrease in activation energy noted for the graphite rods appears to be evidence that in the temperature region between 900° and 1200° C. diffusion and chemical reaction are simultaneously important and a unit of surface deep within the sample does not react as rapidly as one near the periphery of the rod. It would be predicted from this analysis that, at a given reaction temperature, the overall rate of gasification of graphite rods would not be proportional to the total surface area of the sample.

A series of five artificial graphite samples was pretreated by gasifying in carbon dioxide at 1225° C. to develop a large surface area. Each sample was then made to react at a temperature

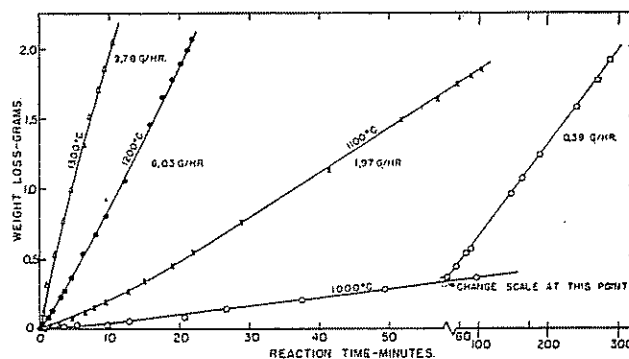


Figure 12. Reaction curves at various temperatures for graphite samples pretreated by reacting of 1 gram at 1225° C.

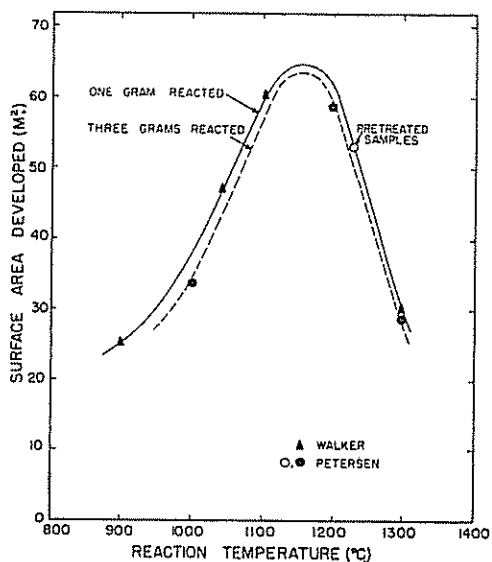


Figure 13. Surface areas developed as measured by low temperature sorption of carbon dioxide on reacted graphite samples

— Areas developed within samples reacted to 1-gram weight loss at constant temperature
 --- Surface areas within samples reacted to 1-gram weight loss at 1225° C. to develop area of 52.5 square meters then 2-gram loss at constant temperature

differing from the pretreatment temperature to determine the effect of the large area on the reaction curves. The attendant surface area adjustment resulting from reaction at the second temperature was subsequently measured.

DISCUSSION

Five graphite samples, initially weighing 9.5 grams, were pretreated by reacting with carbon dioxide at 1225° C. to a weight loss of 1 gram to increase the area of the sample from an initial value of 5.2 to 52.5 square meters in each sample. Subsequently, the samples were made to react to an additional weight loss of 2 grams, at different temperature. Figure 12 shows the reaction curves for the pretreated samples gasified at 1000°, 1100°, 1200°,

and 1300° C. At each reaction temperature except the latter, the curves exhibit an increasing reaction rate which approaches a constant value with time. The final rates recorded on Figure 12 are in good agreement with the rates observed for samples reacted entirely at the same temperature (23). The 1300° C. run began with a greater rate, which decreased with time to a value approximately that of Figure 12 at 1300° C.

Figure 13 is a plot of the surface areas of the samples as determined by low temperature sorption of carbon dioxide. Although each sample started with an area of 52.5 square meters, the magnitude of the areas changed upon subsequent reaction to values characteristic of the latter reaction temperatures—that is, the area of a pretreated sample changed from 52.5 to 28.6 square meters when reacted for a 2-gram weight loss at 1300° C. This is approximately the same area obtained when an unreacted sample is reacted to a 1-gram weight loss at 1300° C.

It is apparent that the observed rates of reaction are not simple, direct functions of the total available surface as determined by the low temperature gas sorption technique, as might be predicted if the reaction was chemical reaction controlled. The complex relationship between total surface area and the observed reaction rate suggests that diffusion within the graphite pore system is rate controlling at reaction temperatures between 900° and 1300° C. Therefore, the concentration decreases with increasing depth of penetration within the graphite rods.

Area developed as a result of partial gasification is perhaps due to development of small shallow pores within the solid, which can be increased or decreased depending upon the temperature at which further reaction is carried out. Such an effect might be accounted for if the initial graphite samples are considered to be a particulate system with the initial 30% porosity largely due to a capillary system between particles. The high surface area developed upon partial gasification then results from a large number of pores developed within these particles. Thus, when samples are partially gasified at one temperature, a shallow pore system develops within the particles, which is removed upon further gasification at another temperature and replaced by a pore system characteristic of the latter temperature. Presumably, the depth and diameter of such a pore system are determined by the intrinsic reactivity of the graphite and the rate at which reactant and products can diffuse in and out, respectively, at various reaction temperatures.

(Reaction of Artificial Graphite with Carbon Dioxide)

UNIFORM GASIFICATION OF ARTIFICIAL GRAPHITE WITH CARBON DIOXIDE AT 1100° C.

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THE reactivities of two forms of carbon in their reaction with carbon dioxide should be compared on the basis of how rapidly a unit surface reacts when the concentration of reactant adjacent to that surface is unity, or the so-called intrinsic reactivity. If the transport of reactant to and the products from the reaction site takes place with a negligible concentration gradient in the pore system, the integral or measured reactivity will be proportional to the intrinsic reactivity and the proportionality factor will be the total accessible area of the sample. However, if appreciable concentration gradients exist within the pore system, the integral reactivity will no longer be proportional to the reactivities (15).

UNREACTED SAMPLES

The size analysis of the petroleum coke flour was determined by a combination of a screen and a microscopic analysis of the -200-mesh fraction. The technique (20) essentially consists of counting the number of particles within designated size intervals and translating the data into a cumulative frequency plot in which the number of particles, N , greater than size r , is known as a function of the radius of the particle, r . To cover the large size range, it is convenient to work with a plot of $\log N$ vs. $\log r$. The weight of the particle system can be expressed in differential form in terms of N and r as: