CATALYSIS OF THE CARBON–CARBON DIOXIDE REACTION BY IRON*†

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Iron in the form of carbonyl iron, ferric oxide, or ferric oxalate solution was added to a spectroscopically pure graphite powder. The graphite was molded in rod-form at 100,000 psi and room temperature. The rate of the reaction of the graphite rods with 1 atm of CO_2 was measured from 900° to 1200°C. Some of the rods were reacted without previous heat treatment above reaction temperature; others were reacted following heat treatment at temperatures between 1400° and 2990°C. For the samples without previous heat treatment, the presence of iron is found to produce a very marked increase in graphite reactivity over that of the pure graphite. Even though heat treatment at temperatures of 1400° and 1635°C does not result in a loss of Fe, it does sharply decrease the catalytic efficiency of the Fe. This catalytic efficiency, in whole or in part, can be restored by a secondary pretreatment in H_2 or O_2 prior to reaction. Heat treatment between 1910° and 2990°C produces an additional decrease in reactivity of the graphite below that which it has following heat treatment at 1635°C. It appears that this additional reduction in reactivity is caused, primarily, by a loss of Fe upon its volatilization from the sample.

I. INTRODUCTION

The oxidation characteristics of graphite are becoming more important as new high temperature uses are found for this material. Impurities can greatly affect the reactivity of graphite[1,2]. When they are removed, the purified product reacts usually at a lower rate[3–6]. Attempts to correlate graphite reactivity with concentration of naturally occurring impurities[7,8] have failed because different compounds have varying effects on oxidation behavior[9–13].

In this work, a start has been made at investigating the catalytic effect of Fe on the C–CO_2 reaction.

II. EXPERIMENTAL

A. *Description of Materials*

The graphite used was National Special Spectroscopic Graphite Powder, Grade SP-1, produced by the National Carbon Company. Its size specification was 65–70% minus 74μ. The base material from which it was made

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‡ Present address Speer Carbon Company, Inc., Niagara Falls, New York.

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was natural graphite. This material was reported to have been heat treated to a temperature of 3000°C[14]. The surface area of the powdered graphite, as measured by adsorption of N_2 at $-196°C$, was 1.8 m^2/g.

Four Fe powders, produced by the decomposition of $Fe(CO)_5$ and obtained from Antara Chemicals, were used as one source of Fe. These powders called L, C, SF, and flocks had average particle diameters on a weight basis of 20, 10, 3, and 0.5μ, respectively. The 20, 10, and 3μ powders were spherical, whereas the 0.5μ powder was twice as long as it was wide. Another source of Fe was chemically pure, minus 44μ ferric oxide. Solutions of ferric oxalate also were used as a source of Fe. The ferric oxalate (purified pearls) was obtained from Fisher Scientific Company.

B. *Sample Preparation*

Two techniques were used to add Fe to the graphite. In the dry method, the proper amounts of graphite and Fe were placed in a plastic container of a Patterson-Kelly "Twin-Shell" blender and mixed for *ca* 20 hr. When using the wet method, a suitable quantity of graphite was outgassed overnight at 105°C and less than 2μ Hg pressure. After cooling to room temperature, an aqueous solution of ferric oxalate was admitted while the graphite was still under vacuum. The graphite was allowed to soak in the ferric oxalate overnight and then the excess solution was filtered off. The impregnated graphite was dried overnight at *ca* 180°C and a pressure of about 2 cm of Hg. After drying, the sample was mixed in the "Twin-Shell" blender for *ca* 6 hr to insure uniformity.

C. *Sample Pelletization*

The mold described by Rusinko and Walker[6] was used to contain the graphite during compression into cylinders $\frac{1}{2}$ in. in diameter and $1\frac{1}{4}$ in. long. Approximately 9 g of graphite were placed in the hardened steel mold and pressed at 100,000 psi, and room temperature. The apparent density of the samples was *ca* 2.13 g/cm^3; the surface area was *ca* 2.3 m^2/g. The increase in area after compaction was probably caused by some breakage of the graphite particles during pelletization. In any case, it indicates that the particle area was accessible to CO_2 during reaction.

D. *Sample Heat Treating*

Some samples were heat treated in a 6 in. i.d. graphite tube furnace to 1635°C. The samples, contained in holders made from "F" processed graphite, were pushed through the furnace at a speed of 1 in./min. The samples reached 1635°C in 30 min and then were brought back to room temperature in *ca* 2 hr. All heat treatments were made in an atmosphere of Ar. Eleven samples, to which no Fe had been added, were placed at random in the various sample holders. They later were reacted and compared to other samples of pure graphite which had not been heat treated. No effect on reactivity due to heat treatment of the pure samples was found.

Some samples were heat treated to higher temperatures in an induction furnace, with an Ar atmosphere maintained throughout the heating and cooling cycle. The samples reached maximum temperature in *ca* 13 min and then cooled to room temperature in *ca* 2 hr.

After heat treating, the samples were faced off on a lathe to a length of 1 in. A $\frac{1}{8}$ in. hole was drilled through the long axis to permit insertion of a mullite support rod used during reaction. The cuttings were saved for spectrographic examination. All samples weighed approximately 6.2 g.

E. *Spectrographic Iron Analysis*

A Jarrell–Ash 21 foot spectrograph was used for Fe analysis[15]. Nickel was used as

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[14] M. Janes, Private communication, 1959.

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an internal standard. The two lines measured with a densitometer were Fe (3047.6 Å) and Ni (3050.0 Å). Both intensities were corrected for background radiation.

F. *Reaction Rate Apparatus*

The reaction rate apparatus has been described previously[6,15]. The sample was suspended from an automatic, recording balance in a tubular reactor. The gases could be passed through two furnaces containing CuO at about 450°C and Cu wool at about 650°C to remove H_2 and O_2, respectively. Activated alumina columns were used to remove moisture. Unless otherwise stated, the samples were preheated at reaction temperature in flowing He for 1 hr before CO_2 was admitted. Upon the admission of CO_2, the flow rate was maintained at a value of about ‘000 cm³/min for 1.5 min in order to flush out the He as quickly as practical. The flow rate then was lowered to 2500 cm³/min and the initial weight reading was taken 0.5 min ater. For some runs, the samples were preheated in He for only *ca* 3 min, which was sufficient time to allow the furnace to return to reaction temperature. Carbon dioxide was then introduced and the initial weight reading was taken just 5 min after the introduction of the sample. The cumulative weight loss was plotted vs. time. Arbitrarily, the reaction rate was taken as the slope of the plot at 20% burnoff divided by the starting sample weight.

III. RESULTS

A. *Reactivity of Pure Graphite*

Reaction rate curves for the pure graphite are shown in Fig. 1. These are typical of the kind normally found for the C–CO_2 reaction, when no catalyst is mixed artificially with the carbon. There is an initial increase in reactivity during an induction period, followed by a region over which the reaction rate remains constant. At some higher burnoff, ne reaction rate will begin to decrease. The length of the preheat period in helium has no effect on these reaction rates.

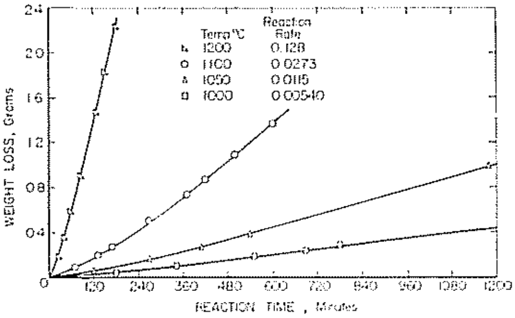

FIG. 1. Reaction rate curves for pure graphite with CO_2.

B. *Effect of Iron Addition from Ferric Oxalate on Graphite Reactivity*

1. *No pre-treatment prior to reaction.* Samples containing 510 ppm of Fe were reacted with CO_2 at 950° and 1000°C, as shown in Fig. 2.

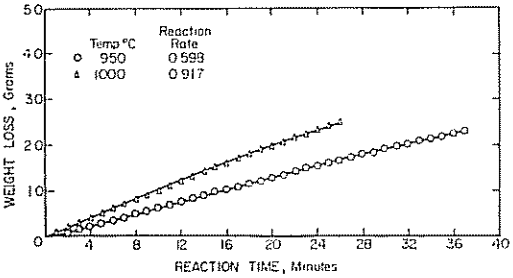

FIG. 2. Reaction rate curves for graphite containing 510 ppm of Fe from ferric oxalate (samples given no pre-treatment prior to reaction).

Weight loss readings were taken 5 min after the sample was introduced into the reactor, as previously described. Despite the large catalytic effect observed, normal reaction rate curves are obtained; i.e. there is an induction period, followed by a region over which the reaction rate remains constant. The addition of 510 ppm of Fe results in a 170-*fold increase* in reactivity at 1000°C over the reactivity of the pure graphite.

2. *Pre-treatment at 1635°C prior to reaction.* Samples containing 510 ppm of Fe were pre-treated at 1635°C prior to reaction. Spectrographic analyses showed that no Fe was lost as a result of the pre-treatment. As seen in Fig. 3, a normal reactivity curve is obtained for reaction at 1050°C. The rate is approximately 100-fold greater than that for the pure graphite. At 1000°C, an extended induction period occurs which lasts, in this case, for about 330 min. During this period the reactivity increases continuously. At the end of the induction period, a sudden break in the reactivity curve occurs, after which a period of constant and high reactivity is found. This type of reaction rate curve was obtained only with samples containing Fe from ferric oxalate, when they were preheated to 1635°C prior to reaction at 1000°C. When the reaction temperature is decreased to 950°C, the reactivity increases continuously and gradually over an extended period. The reaction rate at 950°C for this sample, 0.0188 g/hr/g, can be compared to the rate for the sample containing an equal amount of Fe but not heat treated to 1635°C, 0.598 g/hr/g. A 30-fold decrease in rate is brought about by heat treating at 1635°C.

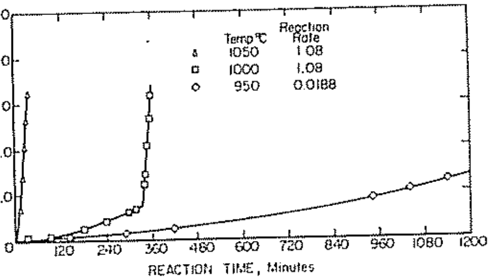

Fig. 3. Reaction rate curves for graphite containing 510 ppm of Fe from ferric oxalate (samples pre-treated at 1635°C prior to reaction).

3. *Pre-treatment at 1635°C followed by pre-treatment in H_2 or O_2 prior to reaction.* It was of interest to see whether the length of the induction period produced by pre-treatment at 1635°C could be changed by a secondary pre-treatment in H_2 and/or O_2. The reaction rate runs following pre-treatment are shown in Fig. 4. A sample was pre-treated for 3 hr in flowing H_2 at 1000°C. During this period there was a weight loss of 0.033 g. At the end of this pre-treatment H_2 was flushed out of the system with He for 3 min, followed by the introduction of CO_2. This pre-treatment results in the removal of the induction period. The sample reacts rapidly as soon as the CO_2 enters the reaction zone. This suggests that Fe need not be in the oxidized state for effective catalysis and possibly that Fe oxide is not a catalyst.

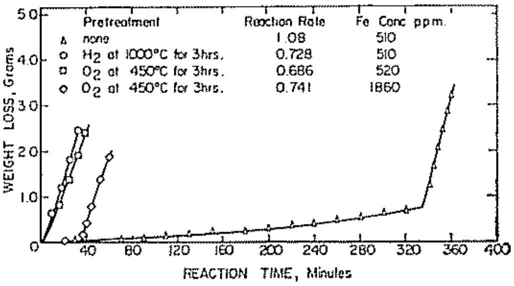

Fig. 4. Effect of pre-treatment in H_2 and O_2 on length of induction period for reaction at 1000°C for graphite containing 510 ppm of Fe from ferric oxalate (samples previously pre-treated at 1635°C).

If the latter were true, pre-treatment of a sample in O_2 should not reduce the induction period. A sample was pre-treated in flowing O_2 for 3 hr at 450°C. This temperature was chosen to minimize the reaction of free carbon with O_2. During the pre-treatment, a weight loss of 0.003 g was measured. After this pre-treatment, the sample was removed from the reactor, the reactor temperature raised to 1000°C, and the system adequately flushed with He. The sample was then placed in the reactor and heated for 3 min in He, followed by the introduction of CO_2. This sample has an induction perio of only *ca* 1 min duration. A similar run was made with a sample containing 1860 ppm of Fe; it was found to yield an induction period of *ca* 35 min. This induction period was less than that for a comparable sample which was not pre-treated in O_2 (induction period of *ca* 100 min).

C. *Effect of Ferric Oxide Addition on Graphite Reactivity*

Figure 5 shows reactivity plots for two samples of graphite, to which 100 ppm of Fe_2O_3 were added. One of the samples was pre-treated at 1400°C in He for 25 hr and then cooled to room temperature in *ca* 5 min. For the reactivity runs, on both samples, the initial weight readings were taken 5 min after the sample was placed in the reactor. As is seen, the reaction rate at 1000°C is decreased very markedly by pre-treatment, falling from 0.814 to 0.0228 g/hr/g —a 35-fold decrease. The sample with no pretreatment reacted 150-*fold more rapidly* than the pure graphite.

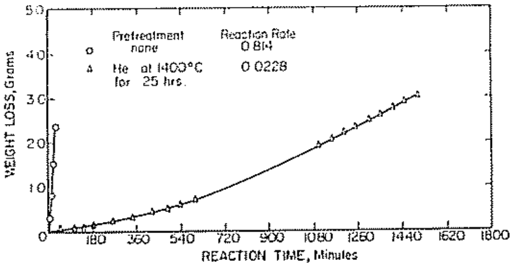

FIG. 5. Effect of pre-treatment on reactivity at 1000°C of graphite containing 100 ppm of Fe from ferric oxide.

D. *Effect of Carbonyl Iron on Graphite Reactivity Following Pre-Treatment at 1635°C*

1. *Variation with iron concentration.* Samples containing varying amounts of 3μ carbonyl Fe were heated to 1635°C prior to reacting at 1000°C. The reaction rates increased with burnoff continuously for each concentration of Fe. Reactivities, at 20% burnoff, are summarized in Table I. Reactivity increases continuously with increasing concentration of Fe, but the reactivity per unit weight of catalyst present progressively decreases.

TABLE I

Effect of Concentration of $3\,\mu$ *Carbonyl Iron on Reactivity of Graphite at 1000°C*

Iron concentration ppm	Reaction rate g/hr/g
57	0.0173
97	0.0199
500	0.0316
1830	0.0447
3900	0.0565

2. *Variation with particle size.* Figure 6 is an Arrhenius plot of log reactivity versus the reciprocal of reaction temperature for samples containing about 500 ppm of Fe. Generally the catalytic effect is increased as the particle size of Fe is decreased. For completeness, the results for samples containing Fe from the oxalate are included. The particle size of this Fe is unknown, but it is suspected to be in the sub-micron range. An activation energy of zero is occasionally obtained

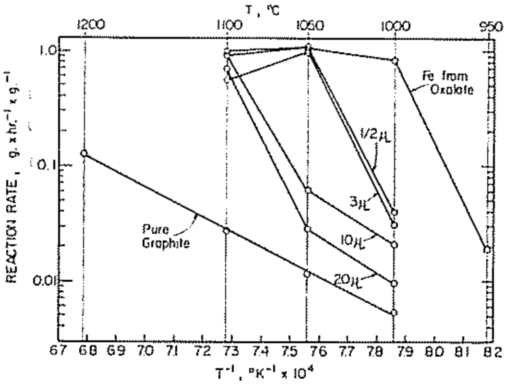

FIG. 6. Arrhenius plots for the C–CO_2 reaction (for both the pure graphite and the samples containing about 500 ppm of Fe).

especially between 1050° and 1100°C. Similar results were found by Okada and Ikegawa[16] and Tuddenham and Hill[10] in their studies of the catalysis of carbon gasification. No satisfactory explanation can be given for this phenomenon at the present time.

Also shown in Fig. 6 are data for pure graphite. An activation energy of 60 kcal/mole is calculated indicating that the reaction is occurring midway between reaction Zones I and II[17].

E. *Effect of Carbonyl Iron on Graphite Reactivity Following Pre-Treatment at Temperatures Between* 1910° *and* 2990°*C*

Samples containing 0.5 μ Fe powder were heat treated in an induction furnace to a series of temperatures between 1910° and 2990°C. After heat treatment, the samples were reacted with CO_2 at 1050°C. Carbon dioxide was admitted 3 min after the sample was placed into a He atmosphere in the furnace. The rate curves are shown in Fig. 7.

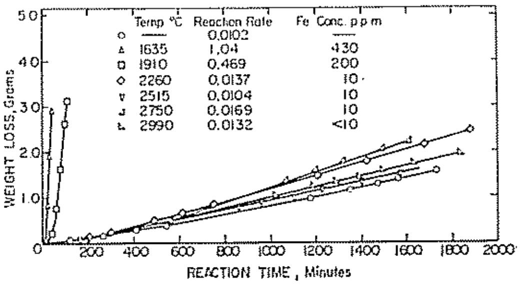

FIG. 7. Reaction rate curves at 1050°C for graphite containing 0.5 μ carbonyl Fe (Samples pre-treated at temperatures between 1635°C and 2990°C prior to reaction).

The drop in reactivity with increasing heat treatment temperature up to 2500°C is parallelled by a decrease in Fe content. Following heat treatment to 2500°C, the reactivity is the same as that for the original graphite. Beyond this temperature, the rate goes through a slight maximum even though the Fe concentration remains essentially constant. Minima and maxima in reactivities for the C–CO_2 reaction have been observed previously in this temperature range[18,19].

IV. DISCUSSION

The extent to which Fe catalyzes the C–CO_2 reaction is dependent strongly upon the previous heat treatment given the sample. This might be expected since the treatment will determine in which chemical and physical form the Fe remains.

In this study, some of the samples were pre-treated by heating to 1635°C. Prior to this heat treatment, the Fe was either in the form of metallic Fe or Fe oxide. Any Fe oxide present undoubtedly was reduced to metallic Fe by the large excess of graphite present during the heat treatment. At 1635°C, *ca* 5.4 wt. % of graphite will be dissolved in Fe at equilibrium[20]. Because of the type of system being studied (Fe particles dispersed throughout a graphite matrix), it is believed that the Fe was saturated with carbon during the heat treatment to 1635°C.

Upon cooling from 1635°C to room temperature, most of the carbon which was dissolved in the Fe probably precipitated out of solution, the carbon atoms diffusing to either grain boundaries or to dislocations within the Fe particles. X-ray diffraction measurements indicate that very little cementite, if any, was present[21].

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[16] J. Okada and T. Ikegawa, *J. Appl. Phys.* **24**, 1249 (1953).

[17] P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin, *Advances in Catalysis*, Academic Press, New York (1959), p. 165.

[18] I. Geller, Ph.D. Thesis, The Pennsylvania State University (1958).

[19] D. O. Baumbach, M.S. Thesis, The Pennsylvania State University (1958).

[20] L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York (1953), p. 419.

[21] The amount of cementite was probably very small because none could be found in samples that contained 10% Fe when examined by X-ray diffraction after heat treating to 1635°C. This is not surprising since *ca.* 5% of a constituent must be present before it can be identified by X-ray diffraction.

For reactivity studies, the samples were heated to temperatures varying from 950° to 1100°C. At these temperatures, the solubility of carbon in Fe increases considerably above that at room temperature. Whereas at room temperature the solubility of carbon in Fe is *ca* 6×10^{-11} wt. %[20], it increases to *ca* 1.3% at 950°C and to *ca* 1.9% at 1100°C[22]. The carbon which diffused back into the Fe at reaction temperature was most likely a fraction of that carbon which precipitated out of solution during cooling from 1635°C to room temperature. It is believed that during the determination of the reaction rates, CO_2 reacted with the carbon in the Fe to remove it. With regard to the decarburizing action of CO_2, it is known[23] that pure CO_2 is a poor decarburizer of Fe. On the other hand, a mixture of CO_2 and CO is a good decarburizer. The reason for this is that CO_2 reacts with Fe to form an oxide film which acts as a barrier against free decarburization. When CO is present, the surface is reduced to the metallic state and, as a result, the CO_2 is able to react with the carbon on the surface of the Fe.

With the above points in mind, the results obtained in this research with samples that were initially heat treated to 1635°C can be discussed. Three different types of reactivity curves were obtained depending on the type of Fe used as a catalyst and the conditions under which the reactivity was measured. In some cases, the reaction rate quickly reached a constant value which was maintained for a considerable length of time. In other cases, the reaction rate continuously increased with time. The third, and most remarkable type of reactivity curve, contained a prolonged induction period followed by a sudden increase in rate to a constant rate period.

These observations appear to be explained by two counter-balancing reactions. The first is the removal of carbon from the Fe by reaction with CO_2. This results in the Fe becoming activated and thereby catalyzing the C–CO_2 reaction. The second is the prevention of the removal of carbon from the Fe by the reaction of CO_2 with the Fe surface to form an Fe oxide barrier to the outward diffusion of carbon. In many cases, normal reaction rate curves with constant rate portions were obtained. This indicates that the removal of carbon by CO_2 was rapid. This type of reaction rate curve was obtained under at least three conditions:

(1) Samples which were not heat treated gave normal curves since the Fe was not poisoned by the carbon.

(2) Heat treated samples gave normal curves when reacted at the higher temperatures because a substantial partial pressure of CO was produced, which kept the surface of the Fe in a reduced state. As a result, carbon diffused quickly to the surface of the Fe and reacted with CO_2.

(3) Samples pre-treated with H_2 or O_2 following heat treatment at 1635°C gave normal curves, since the carbon was removed from the Fe during this pre-treatment.

Reaction rate curves in which the reactivity increased continuously were only obtained at low reaction temperatures with samples previously heat treated to 1635°C. Under these conditions, sufficient CO was not initially generated to maintain the Fe surface in a reduced state. As the CO partial pressure built up in the sample, (as a result of increasing reaction rate) activation of the catalyst slowly progressed, thereby increasing the reaction rate still further.

Long and Sykes[3,9] have postulated a mechanism for catalysis of the C–CO_2 reaction by Fe. They postulated that the gasification of carbon (by desorption of CO from the surface of graphite) would be enhanced if electrons were transferred from the graphite to a catalyst. They suggested

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[22] Metal Progress Data Sheet No. 32 (1946).

[23] W. A. Pennington, *Trans. Amer. Soc. Metals*, Preprint No. 30, 1945, 44 pp.

that transition elements (of which Fe is one) accept electrons because of the non-stoichiometric character of their oxides. Another factor that may be of great importance in catalysis by transition metals is their unfilled *d*-orbitals. As a result of these unfilled orbitals, the transition metals are believed to be able to accept electrons. They, therefore, would be able to catalyze the oxidation of graphite by accepting its electrons and, thereby, enhancing the desorption of CO in a manner similar to that proposed by Long and Sykes. Seith and Kubaschewski[24] showed that dissolved carbon migrates electrolytically in austenite and, therefore, must be in the ionic state. This can be interpreted on the basis of the assumption that the dissolved carbon has contributed its valence electrons to the *d*-band of the Fe and thus has changed into the metallic state. The presence of carbon could inhibit the catalytic activity of Fe by filling up its vacant *d*-orbitals. Upon removal of the carbon by reaction with O_2, H_2, or CO_2, the catalytic activity could be regenerated.

Another possible mechanism for the catalysis of the C–CO_2 reaction by Fe is suggested from the work of Wagner, *et al.*[25] They conclude that CO_2 dissociates over Fe to give CO and adsorbed oxygen atoms. These atoms are probably highly mobile on the Fe surface and could diffuse to a free carbon interface where they would react to produce gaseous CO. It is suggested that the rate of dissociation of CO_2 would depend not only on the composition of the gas phase but also on the composition of the solid phase, in particular the concentration of excess electrons and holes. Perhaps the presence of carbon within the Fe particles decreases the rate of CO_2 decomposition, and thereby decreases the catalytic efficiency of the Fe.

The Fe-carbon system is being studied further. In particular, effects of heat treatment conditions on graphite reactivity are being correlated with the effects of heat treatment on the magnetic susceptibility and thermoelectric power of identical samples.

We appreciate the use of the graphite tube furnace at the Speer Carbon Research Laboratories for heat treating some of our samples. The National Carbon Company kindly donated the spectroscopic graphite powder used in this research.

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[24] W. Seith and O. Kubaschewski, *Z. Elektrochem.* **41**, 551 (1935).

[25] F. Pettit, R. Yinger, and J. B. Wagner, Jr., *Acta Metallurgica* **8**, 617 (1960).