

THE EFFECT OF SUBSTITUTIONAL BORON ON THE KINETICS OF THE CARBON-OXYGEN REACTION

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Abstract—Natural graphite flakes have been doped substitutionally with boron at six concentrations between 6×10^{-6} and 10^{-2} B/C atom ratios. The reactivity of these graphites and of the undoped material with dry and moist O_2 has been studied as a function of temperature (550–650°C), carbon burn-off, O_2 pressure and pre-treatment in water at 625°C. Boronation lowers the rate of carbon gasification in both dry and moist O_2 , despite the fact that it also lowers the activation energy of the reaction. However, boronation also lowers the pre-exponential factor in the Arrhenius expression, apparently because of the formation of liquid B_2O_3 and possibly HBO_2 (in moist O_2) which blocks active sites on the graphite surface. This conclusion is supported by a continuous decrease in specific BET surface area of the graphite at burn-offs above about 10 per cent. The decrease in activation energy of gasification with increasing boronation parallels qualitatively the effect of boronation in lowering the Fermi level of graphite. It is suggested that this correlation supports clearly, for the first time, the Long and Sykes concept that electron transfer between the graphite and an impurity can be important in affecting the rate of gasification of the graphite by an oxidizing gas.

1. INTRODUCTION

Two main theories have been advanced to explain catalysis of carbon gasification by metal impurities[1]: the oxygen-transfer and electron-transfer theories. In the former theory, the metal catalyzes the dissociation of the oxidizing gas into atomic species which diffuse to the graphite surface and gasify carbon as CO and CO_2 with a collision efficiency close to one. In the latter theory, an electron-transfer takes place between the metal and the graphite, which changes the Fermi level (or chemical potential) of the carriers in the graphite. This transfer thereby affects the rates of oxygen chemisorption and carbon gasification, presumably by changing the activation energy. The difficulty with deciding between these two theories is that it is not possible to dope graphite either sub-

stitutionally or interstitially with most metals. The metal resides on the graphite surface where, in principle, it can catalyze carbon gasification by either the oxygen-transfer or electron-transfer mechanism.

It is well known[2–5] that graphite can be doped substitutionally with boron in amounts up to a B/C atom ratio of at least 10^{-2} by heating graphite with boron or boron carbide powders to greater than 2500°C. Studies of the electronic transport properties of such boron doped graphites[2, 4, 5] have shown that the boron acts as an electron acceptor with a high ionization efficiency, which results in lowering of the Fermi level of the graphite with increasing boron content.

The present work investigates the kinetics of the carbon-oxygen reaction for a series of graphites which have been doped substitutionally with boron at six different levels from B/C ratios of 6×10^{-6} to 10^{-2} , in an attempt to correlate kinetic changes with the electronic

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effects of the boron. Thomas and Roscoe [6] have shown that for graphite single crystals, the presence of moisture in the O_2 drastically changes the catalytic effect of the boron. Hence the reaction is studied under both dry and moist O_2 conditions in the present work.

The reaction of O_2 with boron doped graphites is also of considerable practical importance in nuclear engineering, where boronated graphites are frequently used as a control or shielding material in reactors. The interaction of these materials with oxidizing impurities in the coolant gases can be a critical factor in determining reactor life.

2. EXPERIMENTAL

2.1 *The graphite samples*

The preparation and analysis of the samples used in the present work have been described in detail elsewhere [2] and will only be summarised here. Boron powder was mixed with natural graphite flakes (SP-1 graphite containing less than 1 ppm boron) in varying amounts up to 1% (10^{-2} B/C atom ratio), compacted into bars, and then heat-treated to temperatures above 2500°C for 20 min. The boron contents of the resulting materials were determined by chemical and emission spectroscopy techniques. According to the literature [3, 4, 6], this treatment should be adequate to ensure that boron is present in the graphite lattice as a substitutional rather than an interstitial impurity. This was confirmed by electronic transport phenomenon studies [2] and also by annealing one of the samples at 1600°C for 14 hr in vacuum. Under these conditions, any interstitial boron diffuses away [7], but subsequent analysis by emission spectroscopy showed no significant decrease in boron concentration. The graphite rods formed in the preparation were machined into plates $1 \times \frac{3}{8} \times \frac{1}{8}$ in. with a $\frac{1}{8}$ in. hole for suspension from a microbalance. The following B/C atom ratios were studied in the present work, $< 10^{-6}$ (pure graphite), 6×10^{-6} , 6×10^{-5} , 10^{-3} , 2×10^{-3} , 5×10^{-3} , and 10^{-2} (1% boron).

2.2 *The apparatus*

The graphite plates were suspended by a platinum wire from a Cahn R. G. Electrobalance with a sensitivity of 10^{-6} g. The balance was enclosed in a vacuum system with a double-walled Vycor hang-down tube. The outer jacket of the hang-down tube was continuously evacuated by a mercury diffusion pump to minimize the permeation of gaseous impurities into the reaction system. The reaction system could be evacuated to 5×10^{-7} Torr. by a Vac-ion gettering pump backed by a two stage mercury diffusion pump. The sample, suspended in the hang-down tube, was surrounded by a resistance furnace with a constant temperature zone about 4 in. in length. The temperature was controlled to $\pm 2^\circ$ at 950°C by a Leeds-Northrup unit.

Associated with this static reaction system was a Pyrex vacuum line for the preparation and storage of the reacting gases.

2.3 *The gases*

The O_2 used in this work, was the extra dry grade (99.9% purity) supplied in cylinders by Air Products and Chemicals, Inc. This was further purified by passing through a copper oxide tube at 350°C and through towers containing anhydrous and ascarite. The resulting O_2 was condensed in a liquid nitrogen trap. (The maximum O_2 pressure used was 200 Torr.). This gave O_2 with a measured moisture content of less than 10 vppm.

The moist O_2 was prepared from the same gas stream, by bubbling through an ice-water slurry. This gave moisture contents of 2500 ± 200 vppm.

The Ar used was 99.998% purity supplied in tanks by the Matheson Company and was further dried by the same procedure as the O_2 .

2.4 *Procedures*

A standard degassing procedure was adopted for all the graphite samples, namely 950°C at 2×10^{-6} Torr. for 10–12 hr. All the samples were degassed when first placed in the appar-

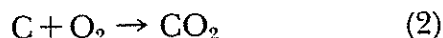
atus and after exposure to the atmosphere when the balance counterweights needed adjustment.

The rates of the carbon-oxygen reaction were determined by continuously recording the weight loss of the sample from the microbalance output. The activation energies were calculated from Arrhenius plots of the rates in the 550°–650°C range at an O₂ pressure of 100 Torr. In this temperature range, the reaction is clearly in the chemically controlled region since, according to the criteria of Walker *et al.* [8], the kinetics were not affected by doubling the sample thickness. The order of the reaction was determined by progressively increasing the O₂ pressure from 2.5 to 200 Torr. at 625°C. The rate at 100 Torr. and 625°C was used to compare the reactivity of different samples at varying degrees of burn-off. Argon BET surface areas were determined gravimetrically in the same apparatus by removing the furnace and immersing the hang-down tube in liquid nitrogen.

3. RESULTS AND DISCUSSION

3.1. Reaction in dry oxygen

The possible reactions for dry O₂ with boronated graphites at 550°–650°C are



It has been suggested [9] that reaction (1) does not occur for heavily doped nuclear graphites (where the boron is not present substitutionally). In the present work, facilities were not available to systematically investigate the composition of the reaction products. However, random mass spectrometric analyses of samples of the residual gas after reaction established that both CO and CO₂ are present in comparable amounts in an atmosphere of predominantly unreacted O₂ (> 95%). It would therefore appear that both CO and

CO₂ are primary products of the oxidation of substitutionally doped graphites. The boric oxide formed under dry conditions remains on the graphite surface in a non-volatile liquid form (melting point 450°C [10]) possibly as a film of carbon-boric oxide glass [11].

Figure 1 illustrates the effect of burn-off on reaction rate (at 625°C and 100 Torr. O₂) for two graphite samples, one with < 10⁻⁶ B/C atom ratio (undoped graphite) and the other with 2 × 10⁻³ B/C (0.2% boron). The data at burn-offs greater than 10 per cent were extracted from subsequent kinetic runs to determine activation energies. Included in Fig. 1 are the Ar BET surface areas. The most prominent feature of Fig. 1 is the marked inhibition of the C-O₂ reaction by the presence of substitutional boron. The steady state rates decrease by a factor of four.

Both the boronated and undoped samples

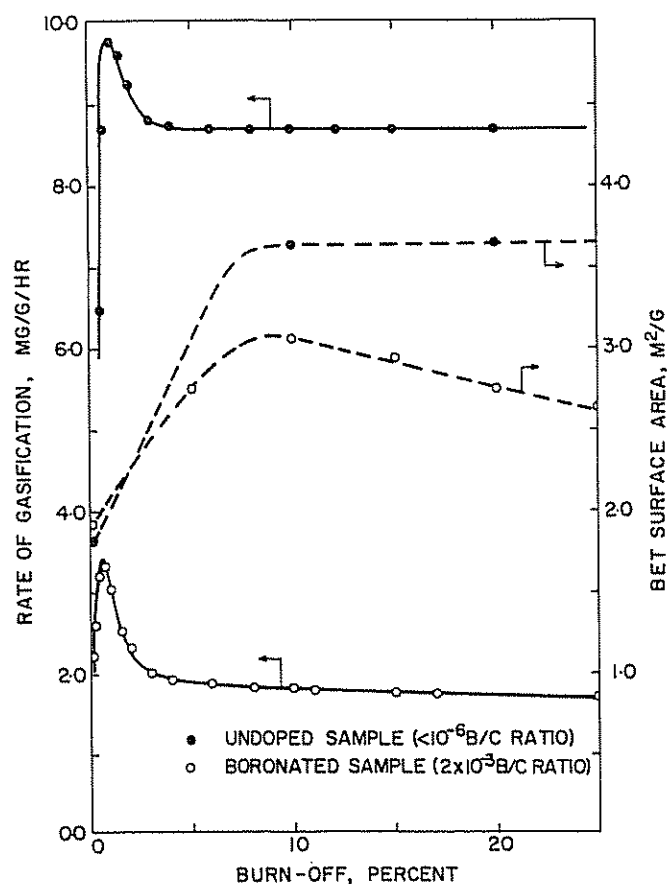


Fig. 1. Variation of gasification rate and BET surface area of graphite with burn-off in dry O₂.

in Fig. 1 exhibit an initial peak rate with a maximum at approximately 1 per cent burn-off, which rapidly decreases to a relatively steady state value by about 6 per cent burn-off. This pattern was observed in every sample studied, although the peak was more pronounced for the boronated samples, if the maximum rate is compared with the steady state value. This initial peak in the reaction rate can be attributed to a combination of factors: namely, burn-off of machine dust from the preparation of the samples, initial rapid reaction at active sites which are not regenerated, and the possible burn-off of exposed boron which may have accumulated at defects and grain boundaries. Unlike the transient peak rates observed by Shelef and Walker[12] for CO_2 on SP-1 graphite, the phenomena observed here could not be reproduced at higher burn-offs by the degassing procedure used in the present study.

The rate of reaction in dry O_2 is not only lower for the boronated sample, but also gradually decreases with increasing burn-off. The undoped sample, however, achieved a steady state rate after 6 per cent burn-off which was independent of burn-off up to at least 25 per cent. The gradual decrease in rate with burn-off was observed for all the boronated samples but was most apparent with the heavily doped graphites. For instance, the rate at 625°C and 100 Torr. for the 10^{-2} B/C atom ratio sample decreased from 3.1 mg/g/hr at 12.3 per cent burn-off to 2.7 mg/g/hr at 25 per cent burn-off. However, there is no evidence to suggest that this effect is due to changes in the activation energy with burn-off, as shown in Fig. 2 where the Arrhenius plots for this sample at three different burn-offs are parallel but progressively lower. Hence, the decreasing rate must be caused by some factor influencing the pre-exponential term rather than the activation energy.

The most feasible explanation of the decreasing rate for the boronated samples is that the progressive accumulation of boric oxide on the graphite surface with burn-off

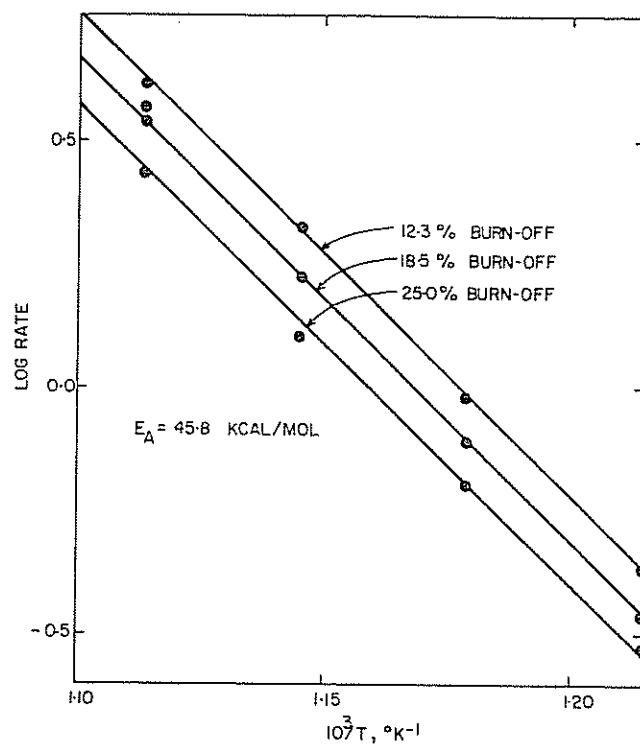


Fig. 2. Arrhenius plots for the reaction of dry O_2 with doped graphite (B/C of 10^{-2}) at 100 Torr. for various burn-offs. Rate is in mg/g/hr.

masks the reaction by blocking active sites [11]. This is supported by the BET surface area data presented in Fig. 1. For the undoped graphite, the surface area initially increases but, analogous to the rate, achieves a constant value by 10 per cent burn-off. The boron-doped sample also showed an initial increase in area, but this was followed by a gradual decrease with increasing burn-off, which also parallels the rate behavior. Every boronated sample studied showed this decrease in area with increasing burn-off, although one sample (5×10^{-3} B/C ratio) did not exhibit the initial increase observed in every other case. (The initial increase in area occurs gradually over the first 10 per cent burn-off, and it is unlikely that it is responsible for the peak rate effect discussed earlier which reaches a maximum at about 1 per cent burn-off.) Thus it appears that there is a causal relationship between the accumulation of boric oxide with burn-off and the decrease in both the rate of gasification and the BET surface area, since neither

effect occurs in the case of the undoped graphite.

The existence of transient peak rates and a rapid increase in BET surface area made it impossible to obtain steady-state kinetic data at low burn-offs. For this reason each sample was burnt-off to at least 10 per cent before the evaluation of kinetic quantities such as activation energies was attempted. The following form of the Arrhenius expression was used: $\text{Rate} = P_{O_2}^n \cdot A \cdot e^{-E_A/RT}$ where P_{O_2} is the partial pressure of O_2 , n is the order of the reaction with respect to O_2 , A is the Arrhenius pre-exponential term, E_A is the activation energy, R the gas constant, and T the absolute temperature. Table 1 presents the kinetic data obtained for the different graphite samples. Both the order and activation energy were independent of burn-off. However, since the pre-exponential term and, hence, the rate varied slightly with burn-off, these quantities are quoted from data obtained in a narrow burn-off range (10–12.3 per cent) in order to compare the reactivities of the different samples. The burn-off at which these data were evaluated for each sample is reported in Table 1. Rates given at 625°C and 100 Torr. provide a simple basis for comparison of sample reactivity.

The order of the gasification reaction for

each sample was determined at 625°C over the pressure range 2.5 to 200 Torr. As noted, the order was independent of boron content over the range of boronation studied. It is in good agreement with results obtained on other polycrystalline graphites [13]. Both the activation energy and the pre-exponential term decrease with increasing boron content. These two effects partially compensate for each other. The rate at low B/C ratios decreases with increasing boron content because $\log(A)$ decreases and E_A is approximately constant, while at higher B/C ratios the rate starts to increase again due to the rapid decrease in activation energy which overshadows the decrease in $\log(A)$. This is shown in Fig. 3, where the rate at 625°C and 100 Torr. (at a burn-off in the 10–12.3 per cent region) is plotted against B/C atom ratio. The fact that the pre-exponential term decreases with increasing B/C atom ratio (Table 1) supports the conclusion reached earlier that its decrease with increasing burn-off for individual boronated samples is associated with accumulation of boron oxide species on the surface.

The activation energies reported in Table 1 are plotted against boron content in Fig. 4. This diagram is similar to Soule's data for the change in Fermi level of graphite single crystals upon boronation [4], as shown in Fig. 5.

Table 1. Kinetic data for the reaction of boronated SP-1 graphite with dry oxygen

B/C atomic ratio	Burn-off (%)	Reaction order	Activation energy (kcal/mole)	$\log(A)$	Rate at 625°C and 100 Torr. (mg/g/hr)
$< 10^{-6}$	11.5	0.60	52.6	12.51	8.0
$< 10^{-6}$	12.1	0.60	52.9	12.63	8.7
6×10^{-6}	12.3	0.60	51.9	12.16	5.8
6×10^{-5}	11.3	0.59	52.7	11.96	2.2
10^{-3}	11.7	0.58	52.0	11.72	1.9
2×10^{-3}	11.1	0.61	51.9	11.70	1.8
5×10^{-3}	10.0	0.60	49.4	11.25	2.6
10^{-2}	10.0	—	47.0	10.77	3.3
10^{-2}	12.3	0.59	45.8	10.56	4.1
10^{-2}	10.0	—	46.7	10.70	3.3

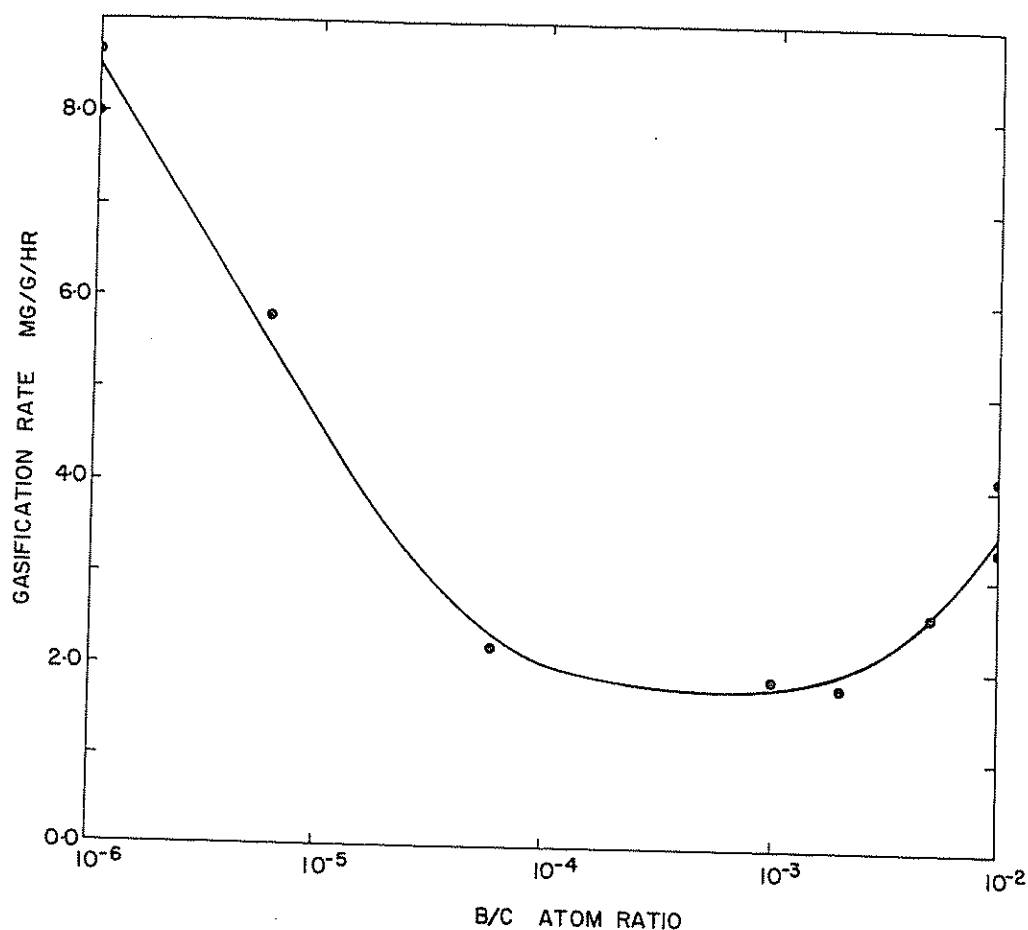


Fig. 3. Change in gasification rate of graphite in dry O₂ at 625°C and 100 Torr. with its extent of boronation. Rates measured in 10 to 12.3 per cent burn-off region.

The fact that the sharp decrease in activation energy starts at approximately 10⁻³ B/C atom ratio compared with Soule's Fermi level crossover at 1.4 × 10⁻⁴ could be explained by thermal excitation which broadens the distribution of the conduction band electrons at the gasification temperatures (550°–650°C) in contrast to Soule's data obtained at room temperature [2]. Changes in the activation energies and Fermi level are of the same order, showing reasonable agreement, when one considers that the Fermi level is a bulk property of the material while the activation energy pertains to localized interactions at specific reaction sites. To the authors' knowledge, this is the first time a correlation between Fermi level changes and activation energy for gasification has been reported in the field of catalysis

of gas-carbon reactions. These results give strong support to the feasibility of the Long and Sykes [14] electron-transfer theory of catalysis but do not eliminate the oxygen-exchange theory as a possible catalytic mechanism either in conjunction or competition with the electron transfer mechanism.

A second, though less favored, explanation of the decrease in activation energy with boronation is that the boron atoms themselves act as active sites and catalyze the reaction. However, Hennig [15] has suggested that substitutional boron atoms in a graphite lattice behave as single lattice vacancies. Hence, one would expect any catalytic effect due to additional vacancies introduced by the boron to be reflected in the Arrhenius pre-exponential term rather than the activation energy.

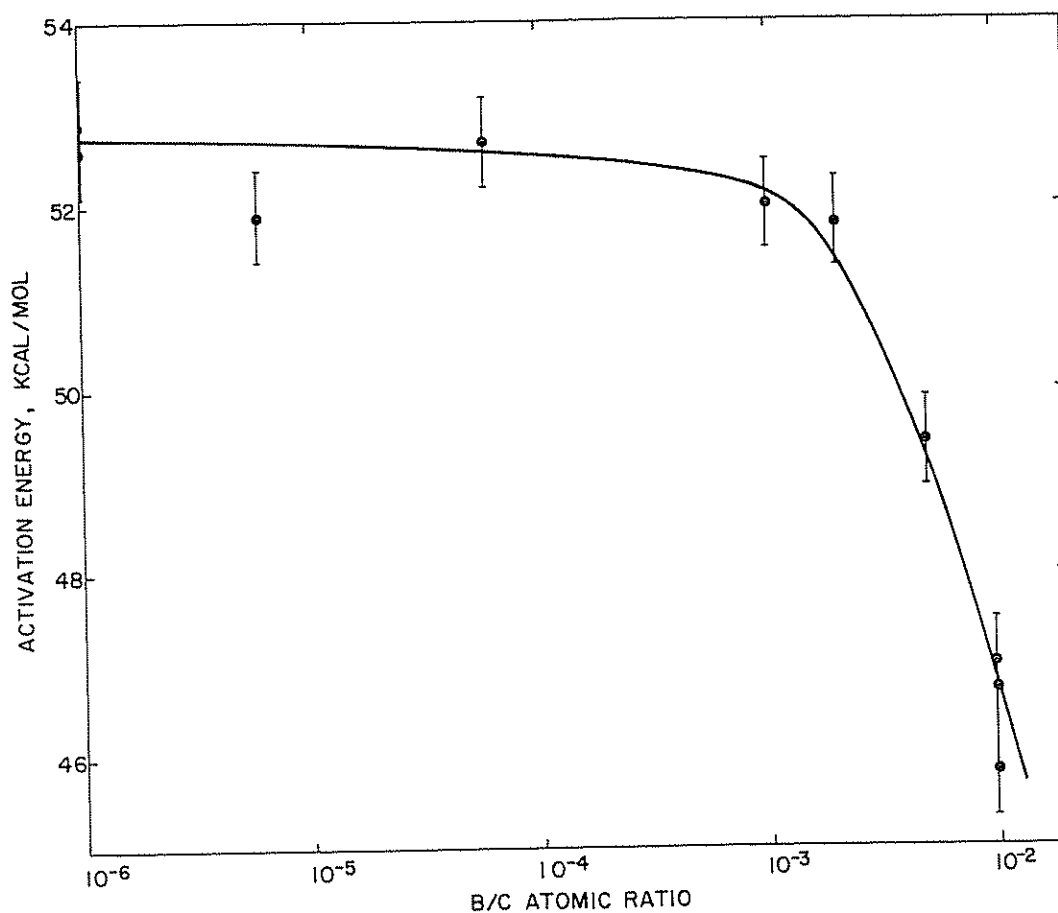


Fig. 4. Change in activation energy for the reaction of dry O_2 with graphite of varying boron content.

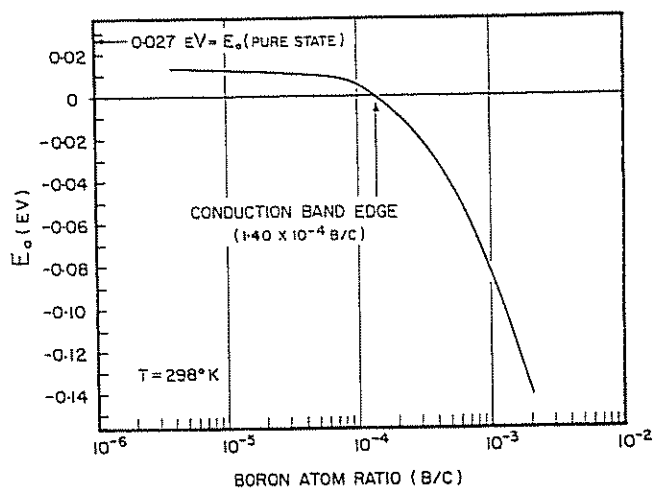
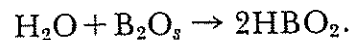


Fig. 5. Fermi level shift with extent of boronation of graphite crystals. After Soule [4].

3.2. Reaction in moist oxygen

Thomas and Roscoe [6] reported that the introduction of moisture to O_2 reacting with

boron-doped single crystals of graphite produced a significant catalytic effect. This is in contrast to the inhibition of the oxidation which they observed in dry O_2 . They concluded that the catalysis in moist O_2 was due to the formation of boric acids on the surface which were volatile at their reaction temperature ($835^\circ C$). Thus there was little accumulation of the boric oxide product which they observed microscopically in the case of dry O_2 . The most likely acid species at the temperatures required for carbon gasification is HBO_2 [10]. That is



In the present work, it was hoped that reacting the boron-doped graphites with moist O_2 (2500 vppm) would also prevent the accumulation of boric oxide on the surface. Thus

Table 2. Effect of burn-off and water treatment on the surface area of boronated graphite (B/C of 10^{-2})

Burn-off (%)	Surface area (m^2/g)	Conditions
0	2.11	Before burn-off
11.6	2.67	After burn-off in moist O_2
11.8	3.39	After water treatment
15.2	2.79	After burn-off in dry O_2
15.4	3.13	After water treatment
17.9	2.71	After burn-off in moist O_2
18.1	3.25	After water treatment

This latter step is accompanied by a weight loss from the sample and visible condensation of boric acids in the cooler regions of the apparatus. No such condensate was observed during the gasification reaction with moist O_2 .

Figure 8 presents the variation in the rate of gasification (at 625°C and 100 Torr. partial pressure of O_2) with burn-off for the 10^{-2} B/C ratio sample under both dry and moist conditions after being treated in water vapor by the procedure described above. As would be expected, the rate decreases rapidly with burn-off, due presumably to a fresh accumulation of B_2O_3 which blocks active sites. The decrease in surface area is not sufficient in itself to account for the steep decrease in observed rate. As discussed in the last section, the behavior in moist and dry O_2 is similar, except that additional retardation in the rate is observed. It should be noted that after the water treatment, the initial gasification rate is higher than the steady state gasification rate for the undoped graphite sample in dry O_2 . Thus the removal of the B_2O_3 by water treatment has resulted in an increase in the $\text{C}-\text{O}_2$ reaction rate for the boron-doped sample compared with the undoped graphite. Woodley [9] also reported enhanced gasification rates after removal of B_2O_3 from his boronated samples by leaching in water. These rates also decreased with increasing burn-off.

Unfortunately, it was not possible in the

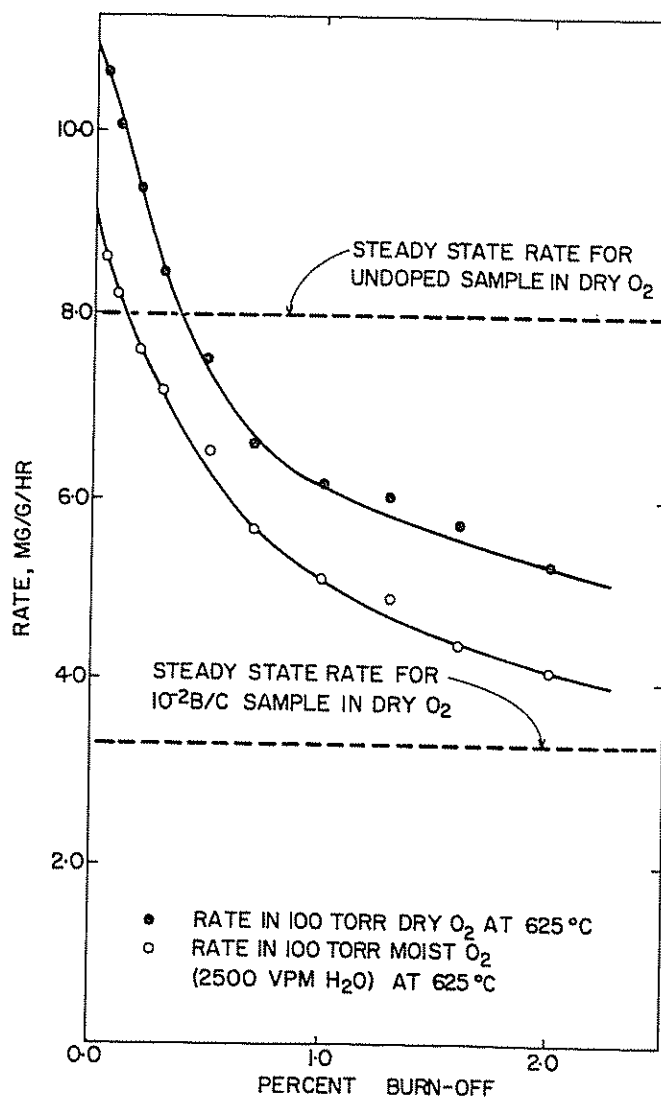


Fig. 8. Effect of water treatment on subsequent gasification rate of a boronated graphite (B/C of 10^{-2}) at 625°C in dry and moist O_2 .

present work to determine activation energies when the rate is faster than for the un-

doped sample. This is because the rate decreased rapidly with burn-off, approaching the rate obtained for a sample with the same boron content which had been reacted in dry O_2 only. However, it is reasonable to conclude that initial catalysis of the C- O_2 reaction for boronated graphites after water treatment is due to the decrease in activation energy, observed in Section 3.1, without the inhibiting effect of accumulated B_2O_3 .

4. SUMMARY

Substitutional doping of graphite with boron does influence the kinetics of the C- O_2 reaction, by decreasing the activation energy. The decrease in activation energy parallels at least qualitatively the lowering of the Fermi level of graphite due to substitutional boronation. This association between electronic and kinetic effects supports the electron-transfer theory of gas-carbon catalysis but does not eliminate the oxygen-exchange theory as a possible mechanism.

Any catalytic effect due to the increase in activation energy is overshadowed by the inhibiting effect of accumulated B_2O_3 which blocks active sites on the graphite surface. This accumulated B_2O_3 results in a progressive decrease in both surface area and gasification rate with burn-off. For polycrystalline graphites under the experimental conditions used in this study, reaction in moist O_2 does not remove from the internal surface the B_2O_3 formed during oxidation. This removal can be achieved by treating the sample in water (20 Torr. at 625°C was used here, though volatilization does occur at lower temperatures). An initial catalysis occurs during subsequent oxidation of a water treated sample, but the rate decreases

rapidly due to further accumulation of B_2O_3 which inhibits the reaction. This initial catalysis presumably results from the decrease in activation energy due to the presence of substitutional boron.

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