

## CARBON-CARBON DIOXIDE REACTION: KINETICS AT LOW PRESSURES AND HYDROGEN INHIBITION

D. L. BIEDERMAN, A. J. MILES, F. J. VASTOLA and P. L. WALKER, JR.  
Department of Material Sciences, Pennsylvania State University, University Park, PA 16802, U.S.A.

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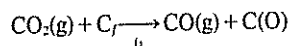
**Abstract**—The gasification of a very high purity natural graphite was studied at temperatures between 960 and 1120°C and at CO<sub>2</sub> pressures below 108 millitorr. For CO<sub>2</sub> depletion up to at least 90%, gasification rates were first order in CO<sub>2</sub> pressure, that is with no inhibition by CO observed. The activation energy for the rate constant for the oxygen transfer step ( $103.5 \pm 5.8$  kcal/mole) agreed within experimental error with that found from kinetic studies at intermediate CO<sub>2</sub> pressures where CO does inhibit the reaction. The rate of the oxygen transfer reaction is markedly inhibited by the presence of low pressures of H<sub>2</sub>. As H<sub>2</sub> pressure is increased up to 3 millitorr, the gasification rate in CO<sub>2</sub> at 1100°C monotonically decreases. Further increase in H<sub>2</sub> pressure, has a negligible effect on rate. From measurements of hydrogen uptake at reaction temperature, it is clear that inhibition is caused by dissociative chemisorption of hydrogen on to active sites. Inhibition by hydrogen is even more marked for the Graphon-CO<sub>2</sub> reaction and is attributed not only to its chemisorbing on carbon sites but also on to impurity catalyst sites. It is doubtful if true rate constants for the C-CO<sub>2</sub> reaction, uninhibited by hydrogen, have ever been reported.

### 1. INTRODUCTION

In the preceding paper [1] the rate of gasification of high purity natural graphite by CO<sub>2</sub> at intermediate pressures was described by Langmuir-Hinshelwood kinetics, the equation having the form

$$\text{Rate} = \frac{k_1 p_{\text{CO}_2}}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}} \quad (1)$$

The rate constant  $k_1$ , which is equal to  $i_1$  for the oxygen-transfer step



was found to have a high activation energy and an accompanying high pre-exponential factor. The high value of the pre-exponential factor does not appear to be reasonable on the basis of classical collision theory or absolute rate theory [1, 2]. At sufficiently low pressures, the terms  $k_2 p_{\text{CO}}$  and  $k_3 p_{\text{CO}_2}$  will be small compared to one and eqn (1) is simplified to

$$\text{Rate} = k_1 p_{\text{CO}_2} \quad (2)$$

This paper describes studies made at low pressures where eqn (2) was operative and, therefore,  $k_1$  could be determined directly. The paper is also concerned with the fact that hydrogen is a strong inhibitor of the oxygen-transfer step in the C-CO<sub>2</sub> reaction.

### 2. EXPERIMENTAL

#### 2.1 Carbons used

For most of the studies SP-1 spectroscopically pure natural graphite was used. It came from the same product lot from the Carbon Products Division of Union Carbide as the graphite used in the preceding study [1]. It is adequately described in that paper. The graphite was molded into plates either 1/16 or 1/32 in. in thickness, as previously described. Following molding, the plates were heat treated to 2500°C in argon to remove impurities possibly added during the

compaction and molding processes. Prior to low pressure reactivity studies, the plates were burned off to 12% weight loss at 1100°C in a 90% CO<sub>2</sub>-10% CO mixture, which passed over the graphite at atmospheric pressure. Previously gasification rates were found to be constant between about 10 and 50% burn-off. The weight of plates used ranged between 0.38 to 0.58 g.

Also used in the study was Graphon, produced by heat treatment of the channel black, Spheron-6, in the absence of oxidizing gases to 2800°C. It was supplied by Cabot Corporation. The as-received Graphon was activated in O<sub>2</sub> to a level of 14.0% burn-off, as described by Laine *et al.* [3]. From N<sub>2</sub> adsorption at 77°K, it was estimated to have a total surface area (TSA) of 97 m<sup>2</sup>/g. From oxygen chemisorption at 300°C, it was estimated to have an active surface area (ASA) of 2.2 m<sup>2</sup>/g, or about 2.3% of the total surface area. From spectrochemical analyses, the total impurity content was <40 ppm, with the major impurities present being Ca and Ti at about 5 ppm each.

#### 2.2 Gases

Gases were obtained from the Matheson Company. The CO<sub>2</sub> was "Coleman grade", having a minimum purity of 99.99 vol %. The H<sub>2</sub> had a minimum purity of 99.9%. The gases were passed through 13X molecular sieves to remove water and then over hot copper turnings at 600°C to remove O<sub>2</sub>. By mass spectrometer analyses, no O<sub>2</sub>, H<sub>2</sub> or H<sub>2</sub>O was found in the CO<sub>2</sub>, meaning the presence of <0.01%.

#### 2.3 Reactor

To follow the rate of the C-CO<sub>2</sub> reaction at low pressures the rates of disappearance of CO<sub>2</sub> and appearance of CO were followed using a CEC Type 21-611 mass spectrometer as described previously [3]. Molded SP-1 graphite plates were suspended from a mullite rod in the 35 mm i.d. vertical quartz reactor tube. Samples of Graphon, ranging in weight from 0.05 to 0.10 g, were held in small quartz boats which were in turn suspended from a mullite rod. The reactor system (11.61 l) was connected directly to the inlet leak of

the mass spectrometer analyzer tube. The amount of gas removed at intervals for analysis had an insignificant effect on the total pressure in the reactor, because of the large reactor volume.

At temperatures above 950°C, a high vacuum cannot be attained in a quartz reactor. Consequently, it was necessary to surround the reactor tube with a quartz jacket. The space between the reactor and the jacket was kept evacuated to a pressure <0.25 millitorr. After outgassing the apparatus for a period of 36 hr at 1130°C to a vacuum better than  $10^{-7}$  torr, a leak rate of <0.1 millitorr/hr at an  $m/e$  of 28 ( $N_2$ ) was found.

Reactivity was found to be sensitive to outgassing conditions. In the studies reported here, samples were outgassed at 1130°C for 12 hr using an oil diffusion pump. If outgassing temperature and time were held constant, reasonable reproducibility could be obtained (see Table 1), even following runs where  $H_2$  was deliberately added to the reactor. Since a constant volume reactor was used in which a small fraction of the total volume was heated to reaction temperature, rate constants were normalized by multiplying by the ratio of the reaction temperature to room temperature in degrees absolute.

### 3. RESULTS

#### 3.1 Reaction of SP-1 graphite in high purity $CO_2$

If eqn (2) is operative, plots of  $\log p_{CO_2}$  vs time should give straight lines, with their slope equal to  $-2.3 k_1$ . Such was found to be the case for all runs made in the temperature range 960 to 1120°C and starting  $p_{CO_2}$  pressures at least up to 108 millitorr. A typical run is shown in Fig. 1. The experimental data for  $p_{CO_2}$  are plotted. In addition,  $p'_{CO_2}$  is calculated from the equation,  $(p_{CO_2})_{initial} - p_{CO}/2$ . Good agreement between the two sets of data is found, which indicates that the concentration of surface oxygen complex  $[C(O)]$  present during the run, produced by way of the oxygen-transfer reaction, was negligible. This is expected to be the case when the reaction is conducted at sufficiently low pressures. That is the rate of gasification is dependent upon the rate at which oxygen complex forms; upon its formation it breaks down rapidly to gaseous CO.

Of interest also in Fig. 1 is the fact that first-order dependence in  $p_{CO_2}$  continues over an extended range of  $CO_2$  depletion. That is,  $p_{CO_2}$  decreased from 72 to 15 millitorr and  $p_{CO}$  increased from 0 to about 114 millitorr. Despite the fact that CO is normally an inhibitor for the gasification of carbon by  $CO_2$ , in this case  $k_2 p_{CO}$  is  $\ll 1$ ; and, therefore, CO does not retard the reaction. From the preceding paper [1],  $k_2$  equals  $8.4 \times 10^6 \text{ cm}^3/\text{mol}$  at 1100°C. Or at a  $p_{CO} = 114$  millitorr,  $k_2 p_{CO} = 1.1 \times 10^{-2}$ .

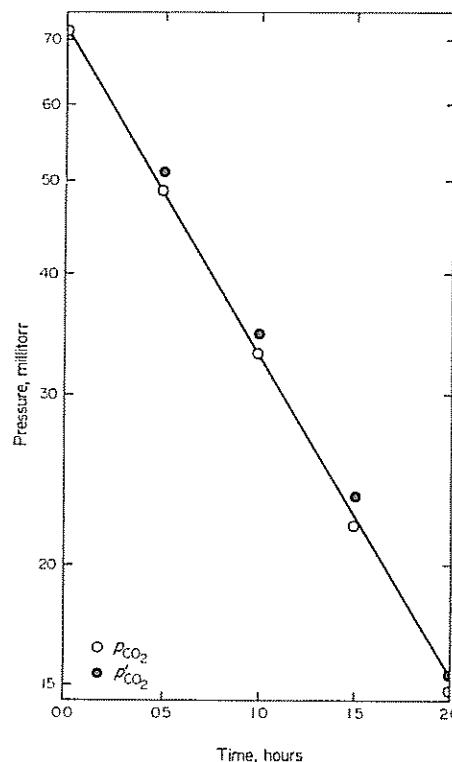


Fig. 1. First order plot for disappearance of  $CO_2$  during SP-1 graphite- $CO_2$  reaction at 1100°C.  $CO_2$  pressure ( $p_{CO_2}$ ) was measured directly and calculated ( $p'_{CO_2}$ ) from measurements of CO pressure.

Results for  $k_1$  obtained in this study are summarized in Table 1. Each value was calculated from at least three separate experimental runs; the majority of them were obtained from five or more runs. A full run could be made with <0.1% carbon burn-off; thus many runs could be made on one sample of SP-1 graphite. In all, there were 35 separate determinations for  $k_1$  made on one 1/32 in. thick graphite sample and seven on one 1/16 in. thick graphite sample. As discussed shortly, at least some of the variation in  $k_1$  between runs is thought to be due to uncontrolled variations in small amounts of  $H_2$  present in the reactor. The temperature dependence of  $k_1$  is shown on the Arrhenius plot in Fig. 2. The line through the experimental points is that given by the method of least squares. The slope of this line yields an activation energy of  $103.5 \pm 5.8 \text{ kcal/mole}$ . The intercept gives a value of  $1.10 \times 10^{19.1} \text{ g cm}^3/\text{g sec mole}$ . Values of  $k_1$  calculated from this line are also given in Table 1.

Table 1. Summary of measured  $k_1$  values for reaction of SP-1 graphite with carbon dioxide

Temperature (°C)	Observed $k_1$ (g cm <sup>3</sup> /g sec mole)	95% Confidence limits (g cm <sup>3</sup> /g sec mole)	Calculated $k_1$ (g cm <sup>3</sup> /g sec mole)
1120	592	± 41	639
1100	390	± 112	370
1080	237	± 8	212
1060	115	± 13	119
1035	50.0	± 2.8	56.3
1010	26.1	± 5.0	25.9
985	13.3	± 2.9	11.6
960	4.60	± 1.43	5.0

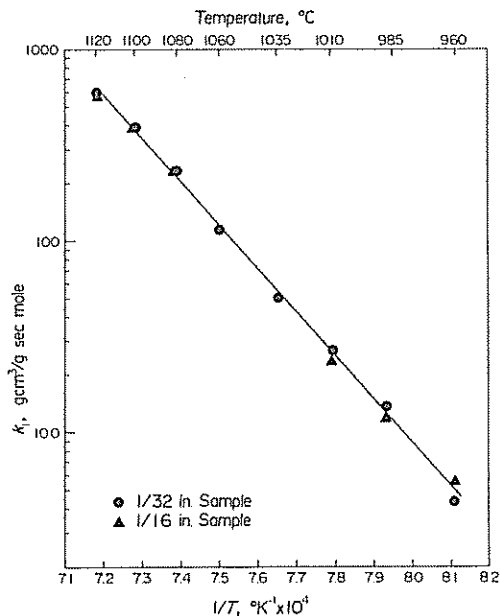


Fig. 2. Arrhenius plot for  $k_1$  for reaction of SP-1 graphite with  $\text{CO}_2$ .

### 3.2 Inhibition by $\text{H}_2$

Hydrogen has long been known to be a strong inhibitor of the  $\text{C-H}_2\text{O}$  reaction [4]. Thus it was of interest to see if hydrogen inhibited the low pressure  $\text{C-CO}_2$  reaction. Studies were conducted at a reaction temperature of  $1100^\circ\text{C}$ . Results of the first run, where 31.9 millitorr of  $\text{H}_2$  were added after 1 hr of reaction in  $\text{CO}_2$ , is seen in Fig. 3. Inhibition is marked. The reaction continues to exhibit first order dependence in  $p_{\text{CO}_2}$ , the new value of rate constant being  $53.7 \text{ g cm}^3/\text{g sec mole}$  compared to the starting value of 670.

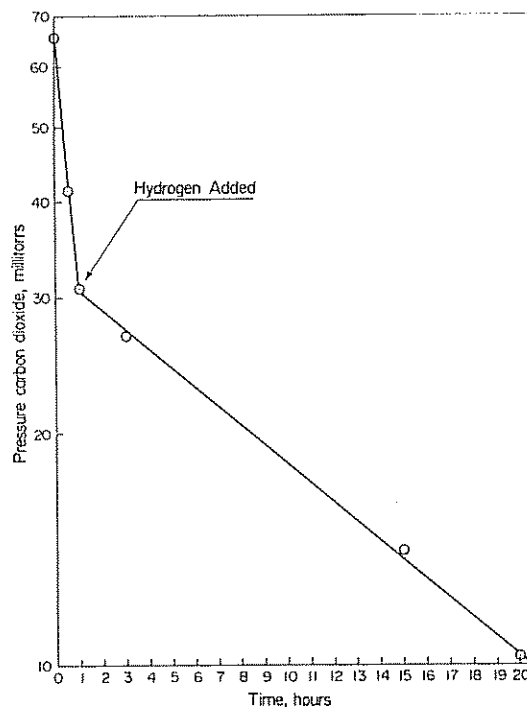


Fig. 3. Effect of addition of 31.9 millitorr of  $\text{H}_2$  on the rate of the SP-1 graphite- $\text{CO}_2$  reaction at  $1100^\circ\text{C}$ .

This high value of  $k_1$  found for no deliberate addition of  $\text{H}_2$ , along with the rather large variation in  $k_1$  sometimes found for repeat reactivity runs supposedly under the same conditions (see results for  $1100^\circ\text{C}$  runs in Table I), led to the monitoring of  $\text{H}_2$  pressure in subsequent runs. Indeed small, but variable, amounts of hydrogen were found relatively early in most reactivity runs. The greater the amount of hydrogen present, the lower was the value of  $k_1$  observed. Results for runs at  $1100^\circ\text{C}$ , at different  $\text{H}_2$  pressures, are summarized in Fig. 4. For pressures up to 0.202 millitorr, no  $\text{H}_2$  was deliberately added during the run. It is seen that  $(k_1)_{\text{app}}$  falls off sharply and monotonically as  $p_{\text{H}_2}$  is increased up to about 3 millitorr. Further increases in  $p_{\text{H}_2}$  result in little further change in  $(k_1)_{\text{app}}$ , it having a value of about  $60\text{--}70 \text{ g cm}^3/\text{g sec mole}$  at  $1100^\circ\text{C}$ .

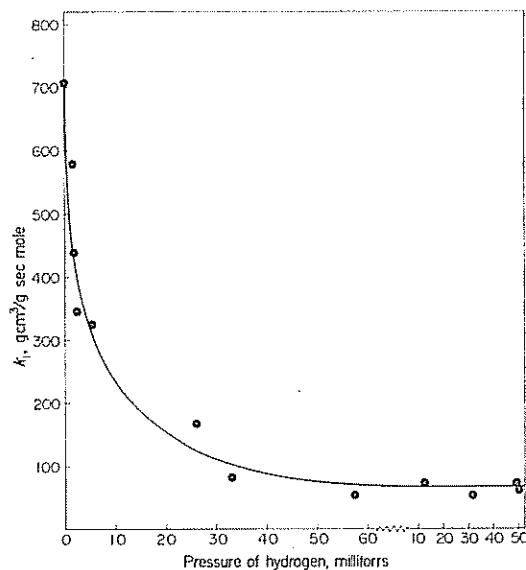


Fig. 4. Effect of addition of varying amounts of  $\text{H}_2$  on  $(k_1)_{\text{app}}$  for the reaction of SP-1 graphite with  $\text{CO}_2$ .

Two points are of interest. First, amounts of  $\text{CH}_4$  formed upon the introduction of  $\text{H}_2$  were negligible. This is as expected since at this low pressure and  $1100^\circ\text{C}$ , the gasification of carbon by  $\text{H}_2$  is most unfavorable thermodynamically [5]. Second, inhibition depends upon the absolute pressure of  $\text{H}_2$  added and not the percentage in the gas mixture. For example, consider two starting mixtures. The first was 108 millitorr of  $\text{CO}_2$  and 5.7 millitorr of  $\text{H}_2$ , or a mixture containing 5.0%  $\text{H}_2$ . The second was 17.8 millitorr of  $\text{CO}_2$  and 2.6 millitorr of  $\text{H}_2$ , or a mixture containing 12.5%  $\text{H}_2$ . For the first mixture, the minimum value of  $52.3 \text{ g cm}^3/\text{g sec mole}$  for  $(k_1)_{\text{app}}$  was found; for the second mixture the value of  $(k_1)_{\text{app}}$  found was  $168 \text{ g cm}^3/\text{g sec mole}$ , that is well above the minimum. Even though the second mixture contained a higher percentage of  $\text{H}_2$ , the  $p_{\text{H}_2}$  was less than that required (about 3 millitorr) to reduce  $(k_1)_{\text{app}}$  to its minimum value.

The reactivity of Graphon in  $\text{CO}_2$  was even more strongly inhibited by the addition of  $\text{H}_2$ . For example, Fig. 5 shows a run at  $950^\circ\text{C}$ . The introduction of 3.34 millitorr of  $\text{H}_2$  reduced the observed rate constant from 2150 to  $13 \text{ g cm}^3/\text{g sec mole}$ . The value of  $k_1$  for the Graphon- $\text{CO}_2$  reaction

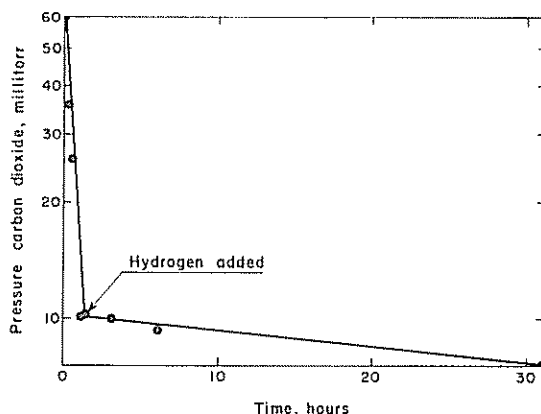


Fig. 5. Effect of addition of 3.34 millitorr of  $H_2$  on the rate of the Graphon- $CO_2$  reaction at  $950^\circ C$ .

prior to  $H_2$  addition is much larger than that for the SP-1 graphite- $CO_2$  reaction at  $950^\circ C$  (that is, about  $3.0 \text{ g cm}^3/\text{g sec mole}$ ). The value for the ratio of  $k_1$ , 716 for the two carbons, is considerably larger than the ratio of their active surface areas from oxygen chemisorption at  $300^\circ C$ , that is 34. This suggests that the  $k_1$  value for Graphon is not only higher than the value for SP-1 graphite because of its higher ASA but also because of its higher impurity content. Impurities are catalyzing the oxygen transfer step. It suggests that a very marked reduction in the value of  $k_1$  for Graphon is not only caused by the chemisorption of hydrogen on its ASA but also caused by chemisorption on impurity sites, thus poisoning their catalytic activity.

### 3.3 Chemisorption of $H_2$

Figure 6 presents the adsorption isotherm of hydrogen on SP-1 graphite at  $1100^\circ C$ . An equilibration time of 2 min was allowed for each adsorption point. Further, slow uptake of hydrogen continued up to at least 1 hr. Even though the isotherm deviates somewhat from Langmuirian behavior, a close estimate of the volume of hydrogen adsorbed in the monolayer ( $v_m$ ) can be estimated from the Langmuir isotherm for dissociative chemisorption, that is

$$v = \frac{v_m K p^{1/2}}{1 + K p^{1/2}} \quad (3)$$

where  $v$  is the volume adsorbed and  $K$  is the equilibrium constant for the reaction  $2C_f + H_2 \rightleftharpoons 2C(H)$ .

A plot of  $1/v$  vs  $1/p^{1/2}$  was linear at the smaller values of  $p$ . The intercept of the plot gave  $v_m = 5.2 \times 10^{-3} \text{ cm}^3 H_2(\text{STP})/\text{g}$ .

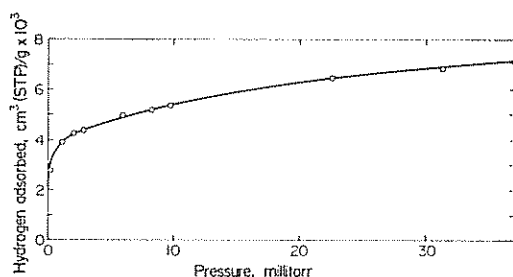


Fig. 6. Isotherm for hydrogen adsorption on SP-1 graphite at  $1100^\circ C$ .

Taking an area of  $8.2 \text{ \AA}^2$  for an active site in the prismatic planes of graphite, it is calculated that a monolayer of hydrogen occupies an area of  $2.3 \times 10^{-2} \text{ m}^2/\text{g}$  of SP-1 graphite. Table 2 summarizes values for the TSA and ASA of SP-1 graphite. It is seen that chemisorbed hydrogen at  $1100^\circ C$  occupies about 30% of the area occupied by chemisorbed oxygen at  $300^\circ C$ . In fact, it may be less than 30% since some carbon sites are thought to chemisorb two hydrogen atoms[4]. As will be discussed later, it also appears that the vacuum attained at  $1100^\circ C$  using a diffusion pump is not sufficient to clean the surface entirely of hydrogen. Thus the isotherm was measured on a surface which was not completely clean.

Table 2. Surface areas from physical and chemical adsorption measurements

Area	Area ( $\text{m}^2/\text{gm}$ )	
	Graphon	SP-1
BET ( $N_2$ )	97	1.8
ASA ( $O_2$ )	$2.24^1$	$6.5 \times 10^{-26}$
ASA ( $H_2$ )	1.25	$2.3 \times 10^{-2}$

From the slope of the  $1/v$  vs  $1/p^{1/2}$  plot which equals  $1/v_m K$ ,  $K$  is calculated to equal  $2.9 \text{ millitorr}^{-1/2}$ . It can be shown that, for reaction at low pressures, with hydrogen inhibition resulting from dissociative chemisorption onto active sites, the gasification rate is given by[7]

$$\text{Rate} = \frac{k_1 p_{CO_2}}{1 + K p_{H_2}^{1/2}} \quad (4)$$

where  $(k_1)_{app} = k_1/(1 + K p_{H_2}^{1/2})$ . This equation well describes the sharp decrease in  $(k_1)_{app}$ , or rate, reported experimentally in Fig. 4. For example, at  $p_{H_2} = 3$  millitorr and taking a value of  $707 \text{ g cm}^3/\text{g sec mole}$  for  $k_1$ , eqn (4) predicts a value for  $(k_1)_{app} = 119$ . The best line through the data points in Fig. 4 gives a value of 111 for the observed rate constant for  $k_1$ .

Figure 7 presents the adsorption isotherm of hydrogen on Graphon at  $950^\circ C$ . This plot is an almost ideal Langmuir isotherm, with adsorption of hydrogen essentially complete

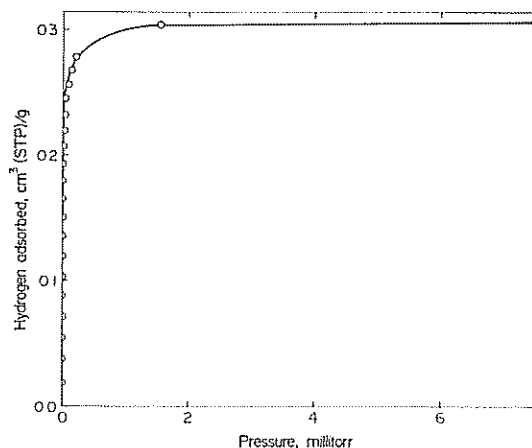


Fig. 7. Isotherm for hydrogen adsorption on Graphon at  $950^\circ C$ .

by a  $p_{H_2} < 2$  millitorr. From a plot of  $1/v$  vs  $1/p^{1/2}$ ,  $v_m = 0.31$   $\text{cm}^3 \text{H}_2/\text{g}$  and  $K = 9.2$  millitorr $^{-1/2}$ . As seen from Table 2, the ASA of Graphon from hydrogen chemisorption at 950°C is estimated as 1.25  $\text{m}^2/\text{g}$ . As with SP-1 graphite, this value is less than that reported from oxygen chemisorption at 300°C.

Equation (4) predicts a value for  $(k_1)_{app} = 121$ , compared to the experimental value of 13, as seen in Fig. 5, for the addition of 3.34 millitorr of  $\text{H}_2$ . This underestimation of retardation, from hydrogen adsorption data on Graphon, again suggests that this carbon-carbon dioxide reaction was being significantly catalyzed by impurities on the Graphon. That is, hydrogen chemisorption on impurity sites effectively removed them from catalyzing the reaction.

#### 4. DISCUSSION

The impetus for conducting the study on the reaction of SP-1 graphite with  $\text{CO}_2$  at low pressures was given by the results in the preceding paper. That is, we wanted an independent check of values for the rate constant  $k_1$  or  $i_1$  for the oxygen transfer step in the C- $\text{CO}_2$  reaction, regardless of which over-all mechanism is operative for inhibiting this reaction by CO. As in the previous study, the activation energy for  $i_1$  has been found to be high, the value in the two studies being equal within experimental error. On the Arrhenius plots in Fig. 8 are shown values of  $k_1$  obtained from this study and from the preceding study of Strange and Walker [1]. Even though the activation energies found from the two studies are equal within experimental error, clearly there is a major difference in the pre-exponential factor for the rate constant. In line with the findings in this study, one possible explanation for this difference is a difference in the hydrogen levels in the reactors during gasification. In this

study, the presence of  $> 3$  millitorr of hydrogen at 1100°C results in a rate constant of about 70  $\text{g cm}^3/\text{g sec mole}$ . The extension of the Arrhenius plot for the data of Strange and Walker to 1100°C approaches closely this point. When greater than 3 millitorr of  $\text{H}_2$  was added during gasification of SP-1 graphite at 1060°C, the value of observed rate constant also is close to the extrapolated results from Strange and Walker as seen in Fig. 8.

In the preceding paper, the pre-exponential term in  $i_1$  was found to be unreasonably high on the basis of collision theory [1]. In this paper, the pre-exponential term in  $i_1$ , as given in Fig. 8, is still higher than that found in the preceding paper and thus even more unreasonable when compared with an upper limit calculated from simple collision theory.

These results point out the great difficulty, and probably the impossibility, of obtaining *true* rate constants for the C- $\text{CO}_2$  reaction. It is impossible to remove the last traces of hydrogen from reactor systems. Certainly outgassing at 1130°C using an oil diffusion pump did not achieve complete removal. In some later runs, an 8 l/sec vacuum ion pump was added to the system. This allowed the attainment of an improved vacuum during outgassing. For example, at 1100°C a vacuum of  $1.9 \times 10^{-6}$  torr could be achieved. Pretreatment of SP-1 graphite under these conditions resulted in subsequent reactivities in  $\text{CO}_2$  up to four times higher than the highest reactivities reported in this study. It is interesting to contemplate the use of higher outgassing temperatures to better clean the graphite and the quartz reactor surface. But in this study, it was not possible to go much above 1130°C under high vacuum during outgassing because of slow collapse of the quartz reactor.

An added difficulty in obtaining true rate constants for the C- $\text{CO}_2$  reaction is the very strong catalytic activity of many impurities for this gasification reaction [8]. Heating of carbons to elevated temperatures of 2500-3000°C is not sufficient for complete removal of metal or metal carbide impurities. Indeed, the high rate of the Graphon- $\text{CO}_2$  reaction in this study as compared to that of the SP-1- $\text{CO}_2$  reaction, after the rates are normalized for ASA, appears to be due to catalysis by impurities. Interestingly it appears that the more the C- $\text{CO}_2$  reaction is catalyzed by impurities in a minimal pressure of  $\text{H}_2$ , the more marked inhibition of the reaction will be upon deliberate addition of significant hydrogen pressure. However, the matter is further complicated in that the extent of hydrogen inhibition is expected to depend upon which impurities are catalyzing the C- $\text{CO}_2$  reaction. If some of the impurities present are only active in a reduced state, such as iron, cobalt and nickel [8], inhibition may be small.

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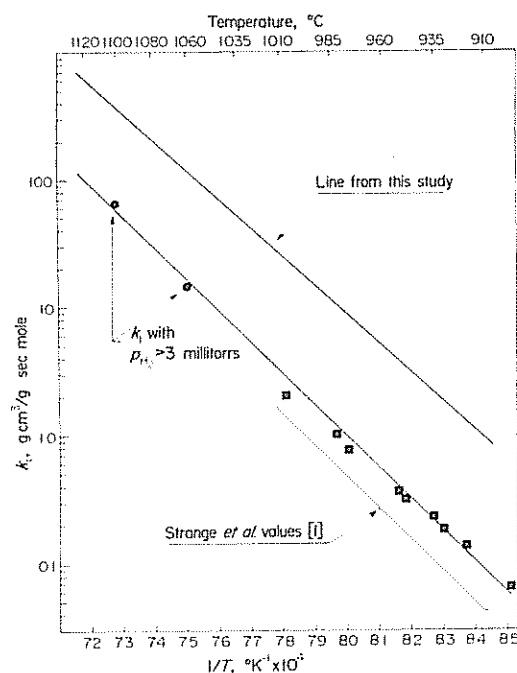


Fig. 8. Arrhenius plots for  $k_1$  for reaction of SP-1 graphite with  $\text{CO}_2$  taken from this study and from Strange and Walker [1]. Solid circles show two data points from this study where  $\text{H}_2$  was deliberately added.

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