

# TRANSIENT PHENOMENA IN THE GASIFICATION OF GRAPHITE BY HIGH-PURITY CARBON DIOXIDE\*

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**Abstract**—A study of the reaction of very pure graphite with thoroughly purified CO<sub>2</sub> has emphasized the role which trace amounts of gaseous and surface impurities can play in the kinetics of carbon gasification. Under these conditions the gasification of well-outgassed graphite proceeds temporarily at rates exceeding by more than an order of magnitude the gasification rates observed in systems to which minute amounts of hydrogen-containing gases and CO have access. The kinetics of this transient gasification have been explained by a model involving two kinds of surface oxides differing in reactivity. One surface oxide is formed on sites exceedingly sensitive to contamination. It possesses a high reactivity, i.e. a relatively short average lifetime on the surface. This is the surface oxide associated with the high rate. The second surface oxide is the more stable species, which is the intermediate in steady-state gasification. The decay of the transient rate is associated with the transition, with time, of the more reactive surface oxide into the relatively stable type. The devised mechanism generates rate-time curves in agreement with the experimental data. The amount of oxides present on the surface after the decay of a transient gasification has been estimated and is satisfactorily accounted for in the proposed model.

## 1. INTRODUCTION

THE COURSE of a gas-solid reaction is greatly affected by the cleanliness of the solid surface which in turn depends on the overall purity of the system. While there have been numerous studies of the Boudouard (C-CO<sub>2</sub>) reaction, investigations under closely controlled purity conditions have been scarce. Recently a series of studies has indicated the importance of minute amounts of impurity in the gas phase on the course of the C-O<sub>2</sub> and C-CO<sub>2</sub> reactions.<sup>(1-13)</sup> The impurities which appear to have the strongest effect on the Boudouard reaction, when present in minute amounts, are those containing hydrogen.<sup>(1)</sup> Special care was taken in this study to keep their amount at a minimum. The Boudouard reaction and its kinetics in the purified system show prominent phenomena not observed heretofore.

## 2. EXPERIMENTAL

### 2.1 Carbon specimens

The carbon employed in this investigation was SP-1 spectroscopically pure natural graphite from

the Carbon Products Division of Union Carbide Corporation. It is supplied in the form of flat flakes which have been purified by a high temperature treatment in halogen gases. The resulting total impurity content is <6 ppm. The spectrographic analysis of the lot used is as follows: Ca, 0-1; Al, 1; Fe, 0-1; Mg, 2-3; Si, 0-2; Na, 1-2, in units of relative intensity. Other elements, specifically sought because of their frequent appearance in carbons and graphites but not detected, were B, Cu, Pb, Mn, K, Ag, Sn, Ti and V. The flakes are 0.3-0.5μ in thickness and *ca.* 30μ in dia.

It was noted in the literature<sup>(14)</sup> that the SP-1 graphite has a remarkable degree of order and can be packed under moderate pressure to give compacts of a density closely approaching that of an ideal single crystal. In our study the graphite was pressed at 100,000 psi and room temperature; 23g portions resulted in parallelepipeds 33/16 × 9/16 × 9/16 in. in size and 2.18 g/cm<sup>3</sup> in density. The density of a compact can be compared with the ideal single crystal density of 2.26 g/cm<sup>3</sup>. The resulting blocks were machined into plates 1 ×  $\frac{3}{8}$  ×  $\frac{1}{16}$  in. (thick samples) or 1 ×  $\frac{3}{8}$  ×  $\frac{1}{32}$  in. (thin samples), with a  $\frac{1}{8}$  in. hole for sample suspension drilled in the center of the width,  $\frac{1}{4}$  in. away from

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one end. Following machining, the plates were heated to *ca.* 2500°C in Ar to remove impurities and some of the defects possibly introduced during compacting and machining.

## 2.2 Gases

The gases were originally Coleman grade CO<sub>2</sub> and C.P. grade CO from the Matheson Co. They were purified from traces of water by successive passage through: a 3 ft column of Linde 13X molecular sieve, a 1 ft column of "Anhydrone", and a 1 ft column of P<sub>2</sub>O<sub>5</sub>. The purification from traces of O<sub>2</sub> was achieved by passage through 1 ft of Cu turnings held at 550°C. The removal of H<sub>2</sub> and other uncondensable impurities was achieved by cryogenic pumping of the CO<sub>2</sub> and CO into cold traps kept at 77 and 63.2°K, respectively, from a 12 l. reservoir at atmospheric pressure, sweeping out the non-condensable gases, re-expanding the free volume of the cold trap into the 12 l. volume five times, followed each time by sweeping out to a total pressure of 10<sup>-6</sup> torr. The purified CO and CO<sub>2</sub> were finally vaporized back into the 12 l. reservoir. It is estimated that the hydrogen impurity in gas purified in this manner is of the order of 10<sup>-2</sup> vppm. The CO and CO<sub>2</sub> when not purified by cryogenic pumping, referred to as non-purified gases in this paper, were assessed to contain 190 and 30 vppm H<sub>2</sub> respectively.

## 2.3 Apparatus

The apparatus consisted of the following sections: (1) gas purification train, (2) freezing-out arrangement for the removal of non-condensable impurities, (3) gas storage, (4) gas-dosing section and (5) reactor section.

The weight decrease of the carbon during its interaction with CO<sub>2</sub> or with CO-CO<sub>2</sub> mixtures was followed by an automatically recording, null-type Cahn R.G. Electrobalance having a sensitivity of 10<sup>-6</sup> g. The balance was enclosed in the vacuum system and operated by remote control. The vacuum in the system was produced by a two-stage Hg diffusion pump and in later parts of the study by a Vac-Ion gettering pump. The graphite plate was suspended from the balance by a Pt wire into a quartz hang-down tube surrounded by a heating resistance furnace. To minimize permeation of external gases at high temperatures into the reaction space, the hang-down tube was cons-

tructed with a double wall, with the annular space between the walls continuously outgassed by a Hg diffusion pump.

The temperature was controlled closely by a Leeds-Northrup unit, the furnace having a constant temperature zone of *ca.* 4 in. in length in which the sample was located. The error in the temperature measurement was ±2°C at 1000–1100°C.

## 3. RESULTS

### 3.1 Description of the transient phenomena

Before each run the samples were burned off to *ca.* 10 per cent weight loss and then outgassed at 1100°C for >10 hr at a pressure of <10<sup>-5</sup> torr.

In mixtures of CO and CO<sub>2</sub>, which were not purified from the non-condensable gases, the gasification rates were the same as observed earlier by STRANGE.<sup>(15)</sup> These rates in the 900–1000°C temperature interval ranged from 3 × 10<sup>-5</sup> to 7 × 10<sup>-4</sup> g/g of starting weight/hr at a typical total pressure of 30 torr and a CO-CO<sub>2</sub> volume ratio of 0.15. The determination of the rate in a typical run required only a very slight burn-off of the sample; and notwithstanding the fact that a closed system was employed, the CO-CO<sub>2</sub> ratio was practically unaffected during a rate determination. The reaction in this case took place clearly in the chemically controlled zone, as was ascertained by applying the criteria of WALKER *et al.*<sup>(16)</sup> The gasification rate as expressed in the above units was essentially constant over a wide range of burn-off, i.e. at least between 10 and 50 per cent.

In non-purified CO<sub>2</sub>, the gasification rate and behavior in the temperature interval, 900–1000°C, was similar, the slightly larger values being attributable entirely to the essential absence of CO, which retards the C-CO<sub>2</sub> reaction as explained by the Langmuir-Hinshelwood type kinetic equation.<sup>(16)</sup> In mixtures of purified CO-CO<sub>2</sub> with an initial CO-CO<sub>2</sub> ratio of 0.15, the reaction again began and proceeded at a similar rate as above which was, at first, surprising. From previous work<sup>(1)</sup> it was expected that the removal of hydrogen from the system should result in a higher gasification rate due to a cleaner reacting surface.

In an attempt to clarify which of the gases might not have been sufficiently purified, the reaction was started in pure CO<sub>2</sub>. The gas was admitted at a pressure of *ca.* 40 torr and the reaction rate

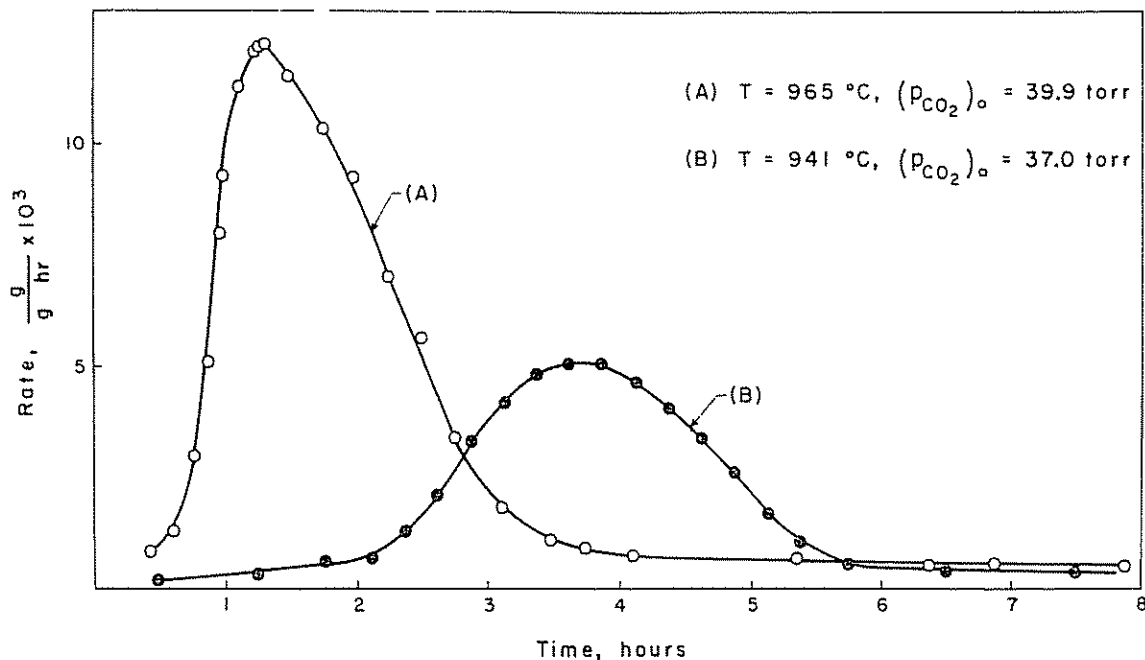


FIG. 1. The transient character of the rate of gasification of very pure and well-outgassed graphite in high-purity  $\text{CO}_2$ .

observed. A significant phenomenon was noted: the rate attained a transient value which exceeded the rate found in the non-purified gases by an order of magnitude (Fig. 1). Subsequently, about 40 runs were made on seven different samples, starting with a purified  $\text{CO}_2$  atmosphere, in which such transients were observed. These runs have been used to elucidate the effects of pressure and temperature on the extent of the transient and the addition of  $\text{CO}$  and  $\text{H}_2$  on depressing the transient.

It is emphasized that when the Hg diffusion pump was used to outgas the system, only *ca.* 50 per cent of the gasification runs started in purified  $\text{CO}_2$  resulted in a transient. When the Vac-Ion pump was employed in the out-gassing, all runs in purified  $\text{CO}_2$  resulted in a high-rate transient. The ultimate vacuum attainable with the Vac-Ion pump was only slightly better (*ca.*  $7 \times 10^{-7}$  torr at room temperature) than that attainable with the Hg diffusion pump ( $10^{-6}$  torr). In runs showing no transient, the rate stabilized almost immediately in the range of values observed with non-purified gases. The same steady-state value of rate was reached after decay of the high-rate transient. The time at which the peak rate in the transient was achieved, the value of the peak rate, and the duration of the transient were not exactly reproducible from run to run at seemingly identical conditions.

For example, at  $965^{\circ}\text{C}$  and *ca.* 40 torr initial  $\text{CO}_2$  pressure, i.e. at the conditions under which most of the runs were started, the value of the peak rate varied in the range  $1.1$  to  $2.4 \times 10^{-2}$  g/g hr. This rate is a factor of *ca.* fifty higher than the rate in the non-purified gases or the steady-state value after transient decay.

Rate curves in Fig. 1 show transients of long duration. The amount of graphite burned off during a transient of long duration reached values up to 7 per cent. Variations in the duration of the ascent and descent of the transient and in the value of the peak rate are thought to be associated with the degree of cleanliness of the reacting system. This fact, in turn, may be influenced by the variation of the permeability of the quartz tubes at high temperatures. The transients were observed both at lower ( $940^{\circ}\text{C}$ ) and higher temperatures (up to  $1070^{\circ}\text{C}$ ). No transient was observed, however, at a temperature of  $916^{\circ}\text{C}$ . The rate of ascent and descent of gasification and the peak rates increased with temperature. The temperature coefficient of the ascent was higher than that of the decay.

It was established in the course of experiments directed towards elucidating the causes of the transient decay that the decay was accelerated both by the addition of  $\text{CO}$  and  $\text{H}_2$  at the peak of the

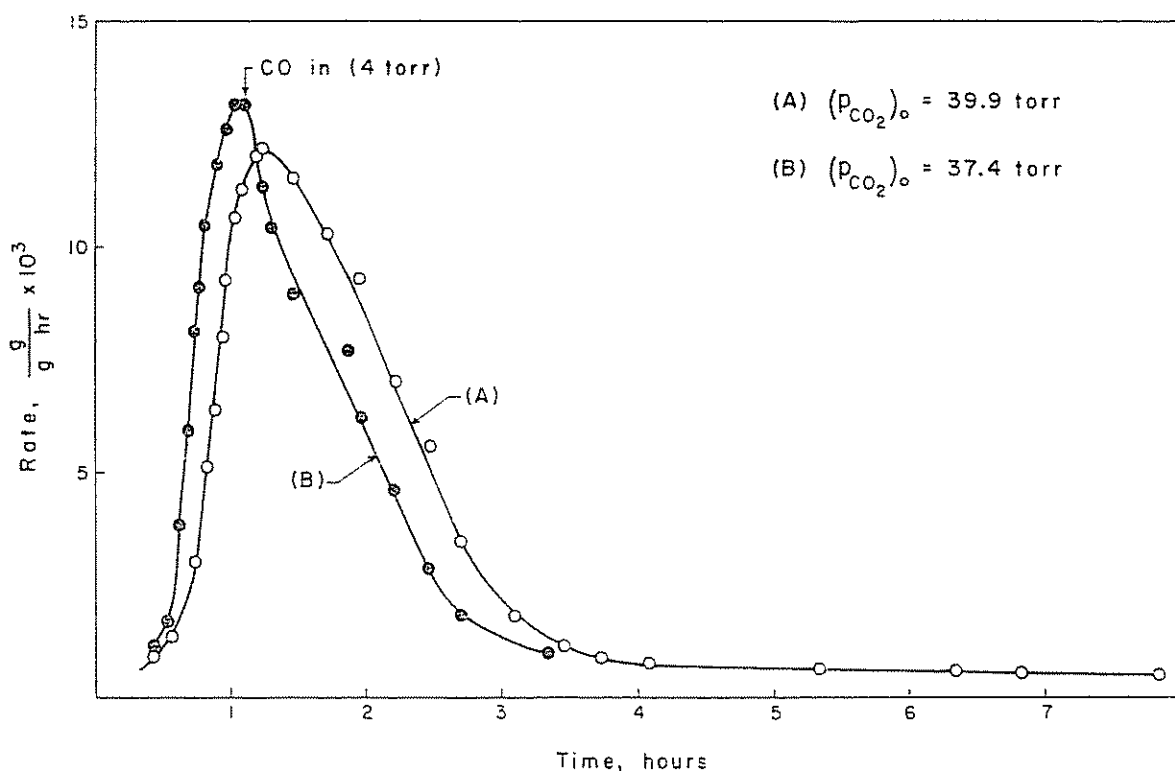


FIG. 2. Effect of CO addition at the maximum of a transient during graphite gasification by  $\text{CO}_2$ , at  $965^\circ\text{C}$ , on its decay (curve B). Curve (A) for a normal transient is included for comparison.

transient. CO is a product of the reaction and it has to be established whether its accumulation in the reactor space is not in itself causing the decay of the transient. The effect of the addition of 4 torr of CO at the peak of the transient to a run which started at  $P_{\text{CO}_2}$  of ca. 40 torr was studied and compared with a normal run (A) as shown in Fig. 2. This amount of CO is roughly equal to that produced in the reactor during the duration of an unperturbed transient. There is an initial drop in the rate, but subsequently the decay parallels that occurring spontaneously, without CO addition. The onset of the spontaneous decay of the transient was largely independent of the CO- $\text{CO}_2$  ratio in the reactor space, being observed over wide ranges of this parameter, i.e. between 0.04 and 0.22. Although CO can prevent the appearance of a transient, it is not a prime factor in the decay of the transient.

The addition of only 42 mtorr of  $\text{H}_2$  at the peak of the transient had a much more dramatic effect [Fig. 3, curve (B)]. It quickly removed the transient, reducing (over a period of a few minutes) the gasification rate to the level observed in non-purified CO- $\text{CO}_2$  mixtures with comparable  $\text{H}_2$  additions.

The transients shown in Figs. 1-3 were obtained following outgassing of the system at  $1100^\circ\text{C}$ , using a Hg diffusion pump. In each case an induction period is observed before a rapid ascent in the rate occurs. When the Vac-Ion pump was used to outgas the system, a detectable induction period was eliminated in those runs where a transient was observed. In fact, at sufficiently high gasification temperatures ( $1037$  and  $1052^\circ\text{C}$ ), the ascending part of the transient could not ever be observed, as seen in Fig. 4. It occurred in  $<2$  min. At  $1014^\circ\text{C}$  the ascent was perceptible; it took 5-6 min. At  $995^\circ\text{C}$  it lasted about 20 min.

### 3.2 Activation energy of gasification during the transient

It is possible in the course of a single run to determine the upper limit of the overall activation energy of the gasification process occurring during the high-rate transient. The technique used was based on the fact that in the broadly peaked, prolonged transients the rate near the peak did not vary by more than 10-15 per cent over a 1-1.5 hr period, during which time at least five rate determinations could be made at descending tempera-

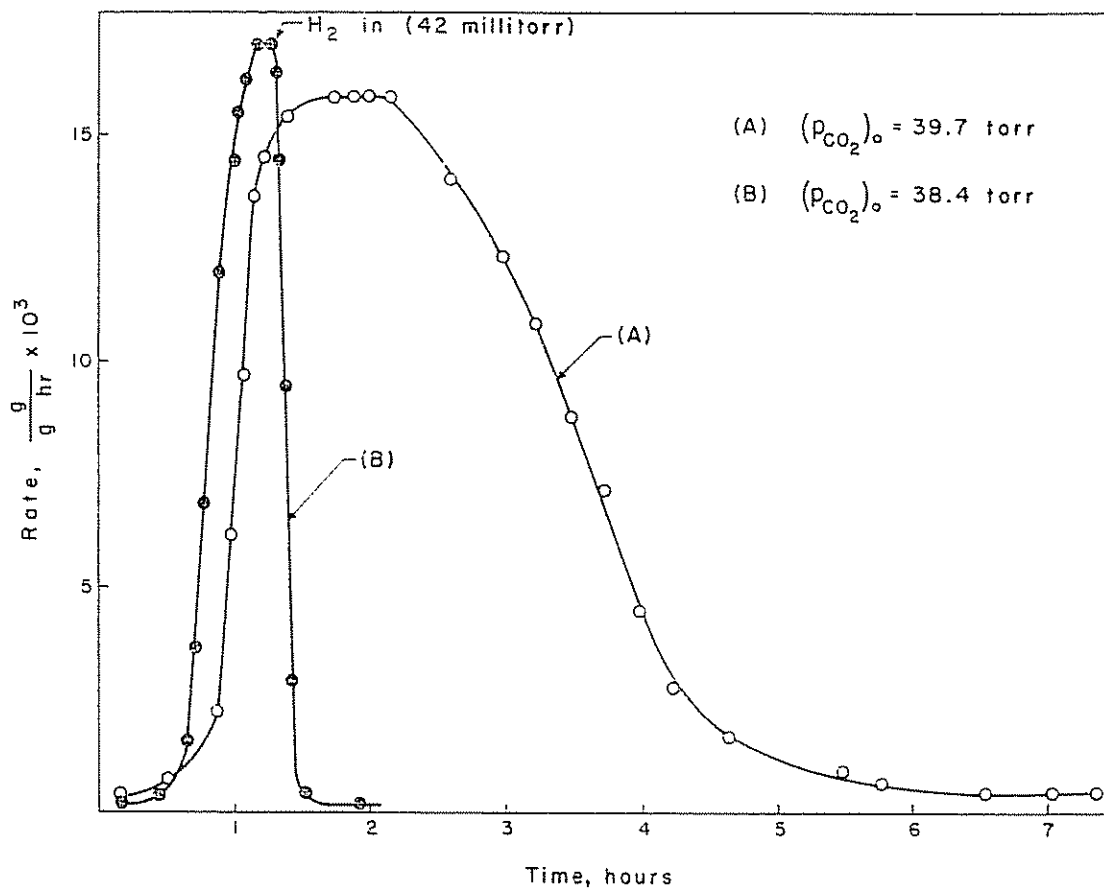


FIG. 3. Effect of  $H_2$  addition at the maximum of a transient during graphite gasification by  $CO_2$ , at  $965^\circ C$ , on its decay curve (B). Curve (A) of a prolonged, undisturbed transient is included for comparison.

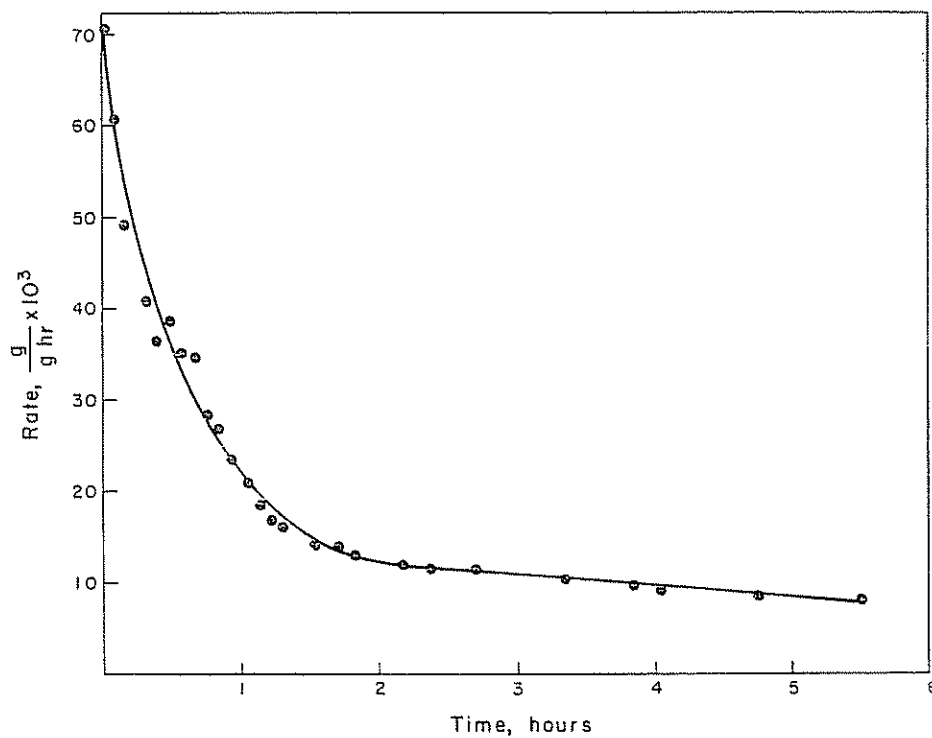


FIG. 4. Segment of a transient graphite gasification by  $CO_2$  at  $1052^\circ C$  and  $(p_{CO_2})_0 = 74.6 \text{ torr}$ . Ascending portion of the transient occurred too rapidly to be measured.

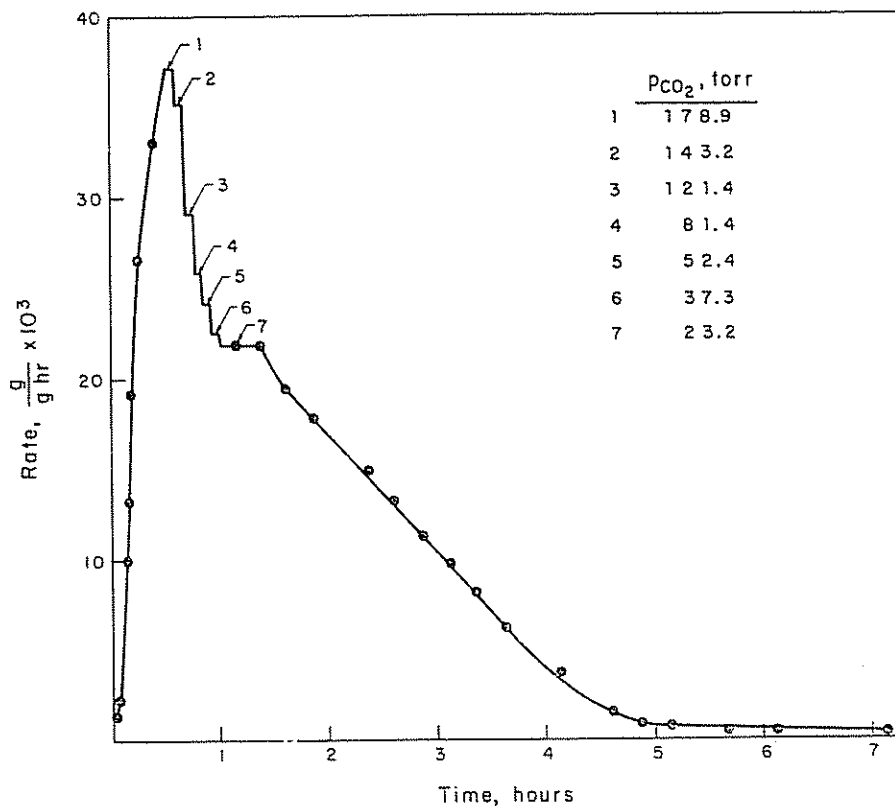


FIG. 5. Effect of incremental decreases of  $P_{CO_2}$  on peak transient gasification rates of graphite at  $965^\circ C$ .

tures. The resulting activation energy is the upper limit, both because the possible rate decay occurring during the determinations and accumulation of CO in the system tend to depress the rate. This approach is preferable to the determination of an activation energy from several runs, however, owing to the previously mentioned variations of the peak rate from run to run. The values of activation energy determined in this manner were quite reproducible, giving a value of  $76 \pm 2$  kcal/mole, as compared with  $87 \pm 2$  kcal/mole determined in this study for the steady-state gasification. The activation energy values refer, in both cases, to the chemically controlled regime.

### 3.3 Effect of $CO_2$ pressure on the transient peak rate

Figure 5 shows an experiment in which the peak rate was attained at a high  $CO_2$  pressure. After the peak was reached, the pressure was decreased stepwise and the rate was determined at each pressure level. Figure 6 shows a plot of rate versus  $P_{CO_2}$  for the same data. The absolute CO pressure formed during the run was highest for the first

rate determination. However, the decrease of the CO pressure in subsequent determinations was more gradual than that of  $CO_2$  owing to the continuous production of CO in the course of the reaction. Hence, the CO- $CO_2$  ratios increased with decreasing  $CO_2$  pressures. The calculated values of CO pressures are given in parentheses in Fig. 6, next to the corresponding experimental points. The absolute CO pressure varies in a rather narrow range, and it is thought that its effect on the reaction order in  $CO_2$  is small. As seen from Fig. 6, a nine-fold decrease in  $CO_2$  pressure decreased the reaction rate by a factor *ca.* two, a part of the decrease of the rate being, possibly attributable to transient decay. This small dependence of the transient rate on  $P_{CO_2}$  is an indication of a high coverage of the reacting surface and of a low reaction order.

### 3.4 Surface area of graphite following fast-rate transients

Surface areas were calculated from Ar adsorption data taken at  $77^\circ K$  using the BET equation. Prior to gasification, the molded graphite plates

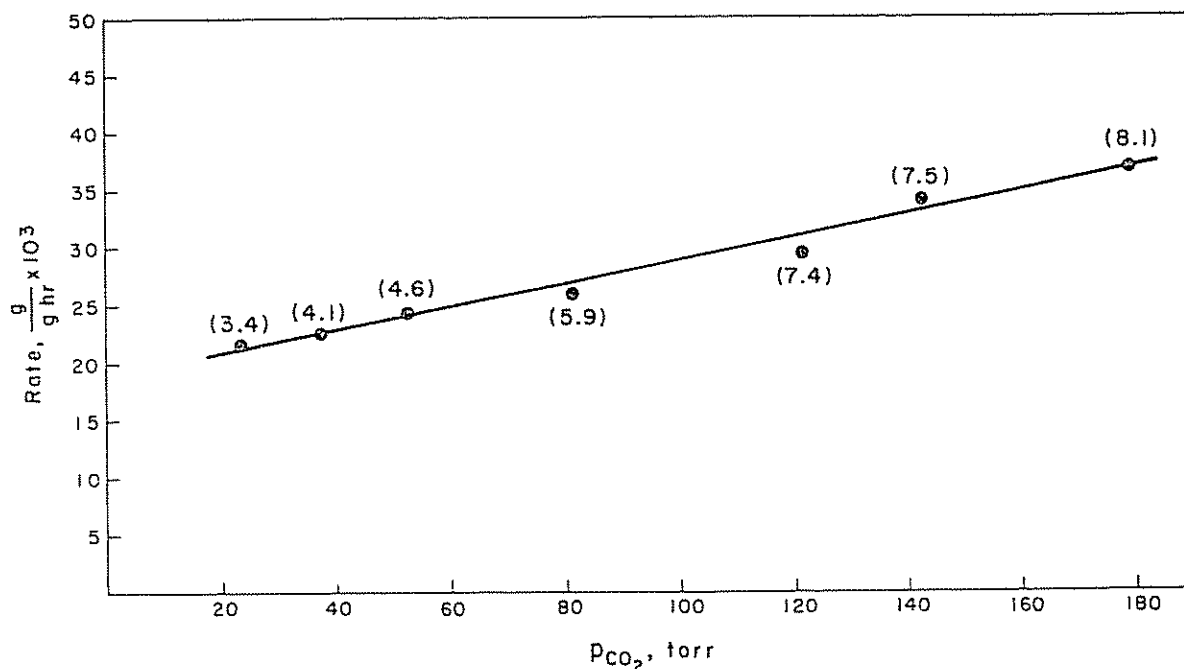


FIG. 6. Change of peak transient gasification rates of graphite at 965°C with  $P_{CO_2}$ .  $P_{CO}$  is given in parentheses in torr.

had a specific area of 1.8 m<sup>2</sup>/g. The area was increased to ca. 3.6 m<sup>2</sup>/g following 10 per cent burn-off in impure CO<sub>2</sub> prior to gasification studies in pure CO<sub>2</sub>. Following gasification through a fast-rate transient, the specific area increased in ca. 8–10 m<sup>2</sup>/g. This increase in area was a result of one transient; additional transients did not result in any further significant increase in specific area.

Calculations show that if gasification of the graphite flakes were occurring only at the edge of the particle, surface area increase due to reduction in particle size would be negligible.<sup>(17)</sup> For example, 50 per cent burn-off would only result in a 2 per cent increase in area. Therefore, it is concluded that significant gasification occurs in the transient region by roughening and etching of the basal plane area. This is not surprising in view of the microscopy studies of THOMAS<sup>(13)</sup> and others. The fact that additional transients (after the first) create little additional area is interesting. It is taken to mean that the number and size of etch pits in the basal plane reach some equilibrium value. Additional gasification leads to pit coalescence and ultimately to removal of entire basal planes.

### 3.5 Desorption studies following fast-rate transients

Figure 7 shows a typical plot for the loss in weight upon outgassing at 1100°C following the normal decay of a fast rate transient. Initially the loss in weight is rapid and the rate of weight loss decreases with time. Following some considerable outgassing time, the rate of weight loss reaches a lower limit and constant value. The slow, constant rate of weight loss is assigned to gasification as a result of a continuous slow leak of oxygen-bearing species through the reactor tube.<sup>(17)</sup> The initial rapid rate loss is assigned to removal of stable oxygen complex present on the graphite surface at the end of a transient run as CO. The amount of this complex can be estimated from the intercept on the ordinate of plots like Fig. 7. For gasification at 965°C, the complex is estimated to consist of  $(1.5-1.8) \times 10^{18}$  oxygen atoms/m<sup>2</sup> of graphite surface. The effect of quenching the transient by H<sub>2</sub> introduction at 965°C (Fig. 3) on the subsequent weight loss upon outgassing at 1100°C was studied. The weight loss was reduced by ca. 75 per cent. This is taken as direct evidence that hydrogen chemisorbed on a large fraction of sites which normally would be occupied by oxygen following the normal decay of a fast rate transient.

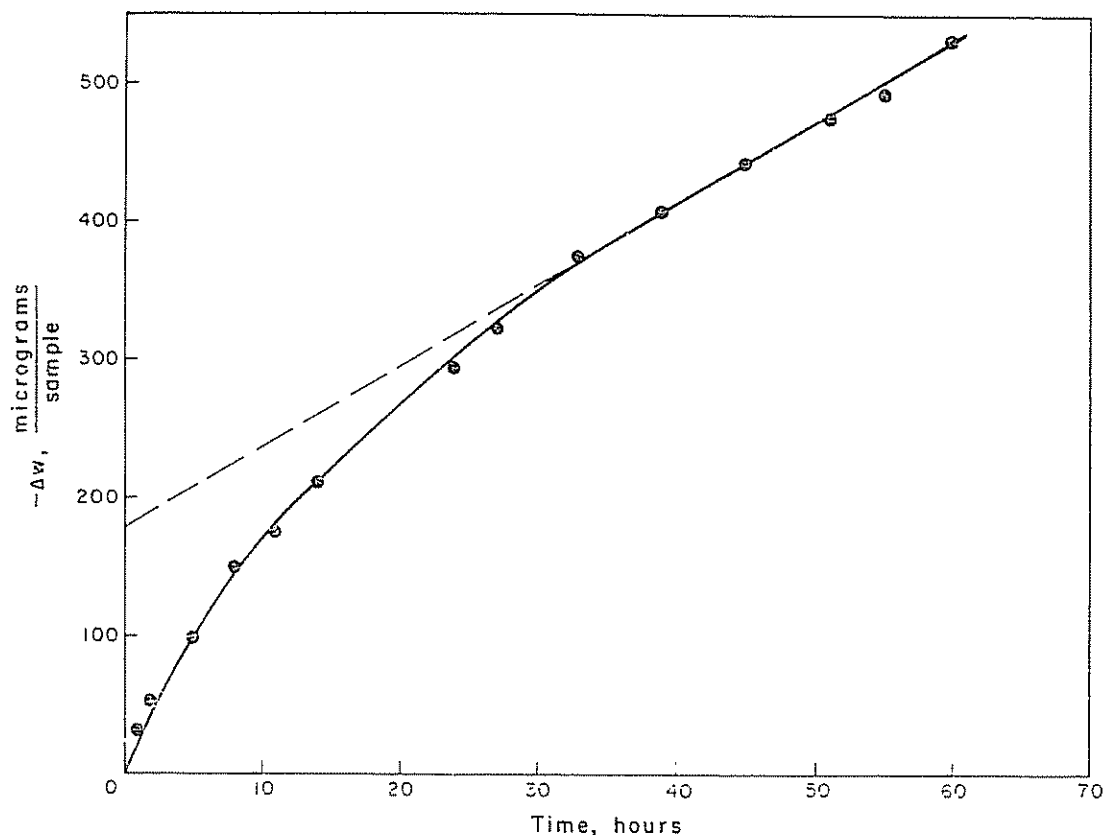


FIG. 7. Observed weight decrease during outgassing at 1100°C following normal decay of a high-rate transient at 965°C. (Vac-Ion pump used for outgassing.)

#### 4. DISCUSSION

##### 4.1 General remarks

Features of the transient gasification by  $\text{CO}_2$  have not previously been investigated thoroughly but have been regarded as an initial period in which irreproducible and unreliable rate measurements are obtained. A careful examination of these phenomena can throw considerable additional light on the gasification reactions, which in their subtle aspects are more complex than suggested by equations derived from steady-state approximations.

It is evident from the experimental results that the magnitude of the observed phenomena is closely associated with the cleanliness of the system. The impurity most detrimental to the inducement of prominent transient phenomena is hydrogen. In gases which were not thoroughly purified, the high-rate gasification was, to all practical purposes, unobservable; the same is true in a gaseous medium which contained initially appreciable amounts of purified CO.

Gasification during the transient rate takes place

on sites which are extremely sensitive to contamination. It is of interest to establish whether these sites belong to the same population partaking in the steady-state gasification and merely represent an extremum in the energy distribution of this population or whether they constitute an energetically and, possibly, structurally different entity. By virtue of the energetic inequality of carbon atoms on the prismatic (edge) planes, the structure of graphite provides *a priori* the possibility that different populations of sites may, in principle, exist. This may be so even if the reaction is restricted only to the edge atoms without invoking the obvious energetic difference between the edge and basal plane atoms. COULSON,<sup>(18)</sup> for instance, distinguished between three main types of carbon atoms on the edge planes: those having (a) unpaired electrons, (b) electron pairs, and (c) partly triple bond character formed by pairing electrons with neighboring atoms. Coulson further states that the actual structure of the edge planes may be much more complicated. It may also be surmised that the SP-1 graphite flakes have a certain degree



of structural imperfection in the form of vacancies, dislocations, surface steps and claw and hole defects. There is ample evidence accumulated in solid-state chemistry that the chemical reactivity of a solid at lattice points near structural defects is, as a rule, higher than that at sites belonging to perfect crystalline arrays. An obvious corollary to the existence of energetically unequal sites on the edge planes of graphite is the possibility of formation of different surface species upon adsorption of the same gaseous species.

The transient phenomenon of fast gasification has also been observed in the C-O<sub>2</sub> reaction and some explanations have been advanced. BONNETAIN<sup>(6)</sup> and BONNETAIN *et al.*<sup>(7)</sup> discard the hypothesis that the reactivity of the freshly outgassed surface is gradually diminished by progressive covering of the surface with a layer of relatively stable oxide. The argument used to support their reasoning is as follows. For the layer of stable oxides to grow during the combustion of successive layers of the graphite, one has to assume that the carbon atoms which emerge on the surface in the course of combustion form stabler oxides than those initially present on the surface after degassing. The requirement seems improbable to the authors; and, therefore, they conclude that the surface-covering hypothesis should be discarded. The explanation favored by Bonnetain *et al.* is that degassing creates on the surface loosely attached carbon atoms, on which unstable, reactive surface oxides are formed. The very reactive carbon atoms are those which were adjacent to carbon atoms removed as CO during outgassing. One can, therefore, expect the amount of carbon burned off before the advent of steady state to be less than one surface layer and independent of temperature and pressure. None of the above conclusions apply to the transients of our study: the carbon gasified during a transient exceeds by ten-fold the monolayer amount and by *ca.* two orders of magnitude the number of edge carbon atoms; it is also dependent on temperature and pressure. The only feature of the above explanation which will be retained in our model is the presence of reactive surface oxides, although not necessarily bound to loosely attached carbon atoms.

The transient phenomenon observed by LANG *et al.*<sup>(19)</sup> is more akin in two respects to the phenomena observed in this study. Firstly, their

transient clearly shows a region of ascending rate (10–20 min); secondly, during the whole transient which decays over 50 min, 6–7 per cent of the sample is burned off. This amount exceeds considerably one monolayer of carbon atoms. In essence, their explanation of the transient phenomenon rests upon accepting diffusion control. That is, Lang and co-workers introduce the concept of micropores, which after degassing participate in the reaction. The rate ascent is caused by the opening of micropores and the decay—by their filling-up with CO, which does not diffuse out. At least two facts appear to militate against this explanation. First, were the opening of the micropores responsible for the ascent, only one ascent would be observed on a given sample in a series of experiments. This is not observed, either in Lang's work or in the present study. Second, it is difficult to see how the water vapor impurity in Lang's study and the hydrogen impurity in our study could cause the annihilation of a transient if the porosity-development argument were to be valid.

#### 4.2 Development of active area upon gasification in transient regime

In the original unburned SP-1 graphite, the amount of edge (active) area is *ca.* 4 per cent of the total surface area.<sup>(20)</sup> Most of the increase of the total area in the course of the fast rate transient has been attributed to roughening of the exposed basal planes and, hence, the exposure of additional edge area at steps and pits. The exposure of intercrystalline boundaries will also be responsible for some new edge area production, if our concept of the particles as an aggregate of aligned crystallites is correct. As a result, one can expect a considerable increase in the edge area–basal area ratio with burn-off.

The number of oxygen complexes on the surface of the graphite determined after a spontaneously decaying transient at 965°C is  $(1.5 \text{ to } 1.8) \times 10^{18} / \text{m}^2$ . The number of atoms on 1 m<sup>2</sup> of edge surface (taking the area occupied by each edge atom as 8.3Å<sup>2</sup>) is  $1.2 \times 10^{19}$ . Assuming that all the edge carbon atoms are covered after the spontaneous decay of a transient by stable oxygen complexes in an O–C ratio of one, it is necessary that *ca.* 15 per cent of the total area be edge area in order to accommodate the experimentally observed amount

of oxygen complex. Another estimate of the extent of edge area is provided by the number of hydrogen atoms chemisorbed at 965°C on an outgassed sample (at 1100°C) which has undergone gasification in a high rate transient. This number is  $3.8 \times 10^{18}/\text{m}^2$  and agrees well with the amount of oxygen complexes on the basis that two chemisorbed H atoms are equivalent to one O atom.

The close agreement between the amounts of desorbed stable oxygen complexes and chemisorbed hydrogen suggests that during the steady-state reaction, which proceeds after the decay of the transient, the overwhelming part of the developed edge area is covered by stable surface oxides. These surface oxides do not contribute significantly to the steady-state reaction rate, as indicated by the fact that the rates on samples with much higher total surface areas (developed during transients) are almost the same as on the initial samples. These relatively stable oxides are not necessarily structurally, i.e. qualitatively, different from those which participate in the steady-state gasification at temperatures above 900°C. They may be similar complexes held more strongly on the carbon. Such an explanation is plausible if it is surmised that the area developed in the transient gasification (or even in the steady state gasification at a slower rate) consists mainly of steps and etch pits where the electron density is higher. This will result in the bond of the oxygen to the carbon (in a carbonyl-like complex) being closer to a full double bond. As shown by STRANGE,<sup>(15)</sup> the average order of the bond in such complexes, which take part in the steady-state gasification, is larger than one but smaller than two.

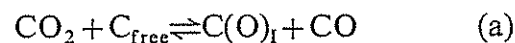
There is, of course, a direct indication that the majority of the stable oxides are held more strongly on the carbon surface than the part participating in the steady-state gasification. This is shown by the necessity to bring the sample to temperatures considerably higher than reaction temperature and to employ relatively long outgassing times for the removal of these oxides.

### 4.3 Mechanism and kinetics of the transient phenomena

It is possible to explain the major phenomena observed in this study by assuming two types of surface oxygen complexes differing widely in their reactivity and by assuming, essentially like

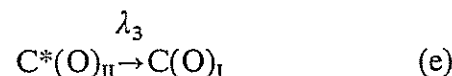
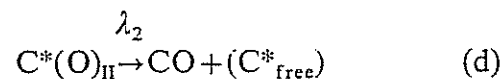
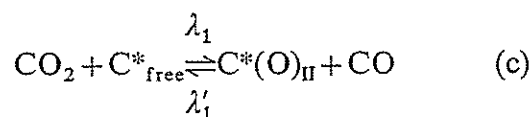
HENNIG,<sup>(21)</sup> that there is a possibility of transformation of the more reactive oxide into the less reactive form. The postulate is that at least two different kinds of sites exist on a thoroughly outgassed carbon, one accommodating a more reactive and the other—a less reactive kind of complex. The estimation of their relative abundance can not be made at present. This drawback can be obviated in the kinetic treatment by the use of simplifying assumptions. The notion of two or more kinds of reactive complexes is not new in the study of carbon gasification.<sup>(4,6,21-24)</sup>

The shape of the transient curves suggests that the observed process may be described by a mechanism in which the more reactive complex plays the role of an intermediate. On the basis of the latest direct evidence,<sup>(15,25)</sup> we adopt the view that Mechanism B<sup>(16)</sup> is operative in the steady-state gasification of carbon by CO<sub>2</sub>. Designating the stabler surface oxide through which the steady-state reaction takes place as C(O)<sub>I</sub>, the set of the chemical reactions, according to Mechanism B is:



The last term in reaction (b) is included to denote a site regenerated when the complex is gasified.

During the transient fast rate, the contribution of the above reactions to the gasification of the carbon can be largely neglected. Thus, we have to consider a more complicated mechanism in which the more reactive complex participates. A set of reactions accounting for the fast rate, in which the more reactive oxide C(O)<sub>II</sub> plays the dominant part, is suggested as follows:



where  $\lambda$  denotes reaction constants. The asterisk on the carbon site indicates that this site is different from the one on which the more stable complex is formed. The last term in reaction (d)

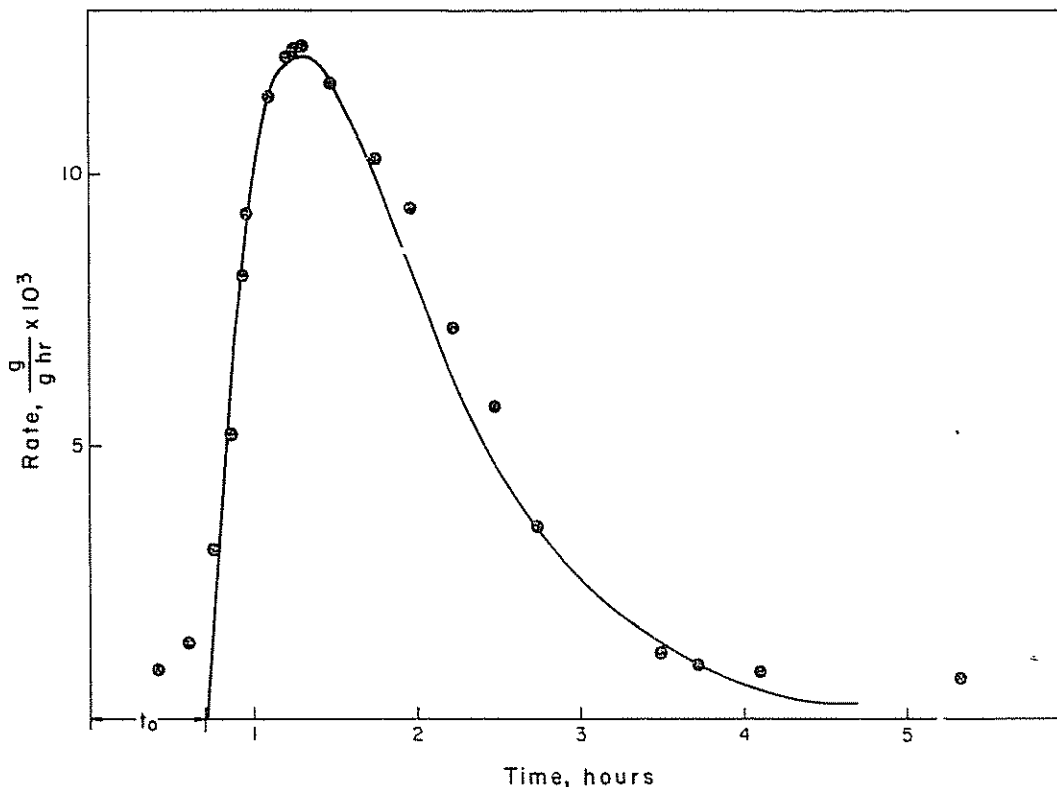


FIG. 8. Fit of data of run *A*, Fig. 1 and equation (2).  $\lambda_3=1.5 \text{ hr}^{-1}$ ,  $t_{\max}=0.57 \text{ hr}$ ,  $(\text{TGR})_{\max}=12.2 \text{ g/g hr}$ ,  $\lambda_1=2.0 \text{ hr}^{-1}$ ,  $\beta_{\max}=0.42$ , and  $F'=28.9 \text{ g/g hr}$ .

shows that a site of the same kind is regenerated when a reactive complex is gasified. Were it not so, the amount of carbon gasified during the fast transient would always be restricted to less than one layer of carbon atoms.

Reaction (e) indicates that the more reactive complex is transformed, in time, into the more stable complex. This process possibly may occur with the participation of the reacting gas, as proposed by HENNIG<sup>(21)</sup> in the case of the C-O<sub>2</sub> reaction. Alternatively, one could write for reaction (e)  $\text{C}^*_{\text{free}} \rightarrow \text{C}_{\text{free}}$ , which would have the same end effect on the disappearance of  $\text{C}^*(\text{O})_{\text{II}}$ , implying only that surface rearrangement is related more to the rearrangement of the graphite lattice than to the rearrangement of surface oxides. As discussed in the previous section,  $\text{C}(\text{O})_{\text{I}}$  formed by reaction (e) may be at the very stable end of the energetic distribution of such oxides and, consequently, does not contribute to reaction (b). Back reaction (c) is relatively unimportant but can not be disregarded altogether, as seen from the slight effect on the rate of the addition (or removal) of CO at the peak of a transient.

To be able to treat the kinetics of the transient by this model, we also assume  $\lambda_2 < \lambda_1$ . This implies that the fast gasification should be close to zero order in CO<sub>2</sub>. That this is essentially the case is shown by the relatively small effect of the CO<sub>2</sub> pressure on the gasification rate in the transient period (Fig. 6). Thus, the gasification rate during the transient is determined primarily by the desorption reaction (d), with the gasification rate directly proportional to the surface concentration of  $\text{C}^*(\text{O})_{\text{II}}$ . That is, the transient gasification rate  $(\text{TGR}) = F[\text{C}^*(\text{O})_{\text{II}}]$ , where  $F$  is a proportionality factor closely associated with  $\lambda_2$  and  $[\text{C}^*(\text{O})_{\text{II}}]$  is the concentration of the reactive complex.

Neglecting reaction (c'), the build-up of the  $\text{C}^*(\text{O})_{\text{II}}$  oxide is determined by reaction (c) only and the decay by reaction (e) only. From the theory of consecutive first order reactions,<sup>(26,27)</sup> we can write for the concentration of the intermediate as a function of time<sup>(17)</sup>

$$\frac{[\text{C}^*(\text{O})_{\text{II}}]}{\text{C}_0^*} = \frac{\lambda_1}{\lambda_3 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_3 t}) \equiv \beta \quad (1)$$

where  $\text{C}_0^*$  is the initial, and unknown, amount of

C\* sites on which the C\*(O)<sub>II</sub> complexes can be formed. Both reactions (c) and (e) may not be first order but may be considered as such at the large prevailing excess of CO<sub>2</sub>. As seen,  $\beta$  is the fraction of the population of C\* sites covered by the C\*(O)<sub>II</sub> at any time during the transient. Combining TGR with equation (1) we obtain

$$\text{TGR} = F' \beta \quad (2)$$

where  $F' = F C^*_0$ .

It now remains to evaluate  $\lambda_1$ ,  $\lambda_3$  and  $F'$  in order to compare the experimental data with those predicted by the model. This may be done by a trial and error fit, but some properties of  $\beta$  make it possible to evaluate approximately the constants from experimental data. The function  $\beta(t)$  passes through a maximum; the values of  $\beta$  and  $t$  at the singular point are:<sup>(26,27)</sup>

$$\beta_{\max} = (\gamma)^{\frac{\gamma}{1-\gamma}} \text{ and } t_{\max} = \frac{\ln \gamma}{\lambda_3 - \lambda_1}$$

where  $\gamma = \lambda_3/\lambda_1$ . By disregarding the induction time ( $t_0$ ), if present in the transient, the experimental  $t_{\max}$  can be read-off from the rate-time curves. The value of  $\lambda_3$  is estimated from the decay sides of the transient curves, where both the effects of rate ascent and steady-state reaction are considered to be minimal, in the following manner. In this portion of the curve, the time in which the rate decreases to half its value is noted as  $\tau_{\frac{1}{2}}$ ; and (from the theory of first order reactions)  $\lambda_3 = \ln 2/\tau_{\frac{1}{2}}$ .  $\lambda_1$  is then calculated from the experimental  $t_{\max}$  and  $\lambda_3$ ;  $\beta_{\max}$  is evaluated by using the values of  $\lambda_1$  and  $\lambda_3$ . The proportionality factor  $F'$  is taken as  $(\text{TGR})_{\max}/\beta_{\max}$ .

A typical fit of the experimental data to the line drawn by the proposed model is presented in Fig. 8. For the transient runs at 965°C, where fitting was investigated,  $\beta_{\max}$  varied from 0.42 to 0.63 and  $F'$  varied from 20.6 to 51.0 g/g hr. The variation in  $F'$  is associated mainly with the run to run variations of  $C^*_0$ , i.e. in the available number of sites on which the more reactive complex is capable of forming. The variation in  $C^*_0$  in turn is an outcome of the varying, uncontrollable amounts of residual impurities.

The prominence of a transient is strongly dependent on  $\gamma(\lambda_3/\lambda_1 \text{ ratio})$ ;<sup>(26)</sup> with the increase of  $\gamma$ ,

$\beta_{\max}$  decreases. Hence, when  $\lambda_3 \gg \lambda_1$  the transient will disappear altogether because  $\beta \rightarrow 0$ ; at  $\lambda_1 \gg \lambda_3$  the C\* sites will be covered immediately and the decay will begin at  $t=0$ . The first situation is observed at 916°C, where no transient can be induced. The second phenomenon prevails at 1053°C (provided that the induction period is eliminated by the use of the Vac-Ion pump). This implies that the activation energy of the rate constant for the ascent ( $\lambda_1$ ) is significantly larger than that of the decay ( $\lambda_3$ ). If one pictures the ascent as related to the act of chemisorption and the decay as associated with a surface rearrangement, a higher activation energy may be expected for the former.

The initial period during which the rate increase is slow, as observed when the system is outgassed by the Hg diffusion pump, can be regarded as an induction period associated with residual impurities. According to BENSON,<sup>(28)</sup> small amounts of impurities are frequently the cause of induction periods noted in complex reactions. Any explanation as to exactly how the impurity is hampering the ascent must, at this stage, be based on speculation. It is believed that the inability of the transient rate to materialize in mixtures of CO<sub>2</sub>+CO is related to the same tendency of any impurity to hamper the ascent, i.e. the buildup of the more reactive complex. At the higher end of the temperature range studied (1070°C), the fast rate materialized in the non-purified CO<sub>2</sub>, although only after a prolonged induction time. The transient in the purified gas at the same temperature took off more rapidly; this and the fact that the Vac-Ion pump degassing tends to eliminate the induction period are experimental facts in strong support of the above expressed view regarding the impurity-related nature of the induction period.

At the higher end of the temperature range, the transient could not be quenched easily by H<sub>2</sub>. This indicates that at higher temperatures the sites responsible for the fast rate do not adsorb hydrogen strongly. Indeed the fact that outgassing at 1100°C leads to the uncovering of these sites, even if previously contaminated by hydrogen, is in line with this reasoning. It is possible that not all such sites are uncovered at 1100°C. The desorption at this temperature is a prolonged process, as attested by the long outgassing periods necessary for the observation of a subsequent transient or for the removal of the surface oxides.

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