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*Manuscript received April 29, 1963; revision received October 9, 1963; paper accepted October 10, 1963. Paper presented at A.I.Ch.E. Houston meeting.*

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# Graphite Oxidation at Low Temperature

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Although carbon oxidation processes have been an integral part of our industrial economy for many years, a complete understanding of the reaction kinetics has lagged behind practical utilization. Complications arising from the properties of solid carbon and from interfering side reactions have made the study of initial oxidation steps difficult. Knowledge of the mechanism would be of interest in fuel bed design for energy generation or chemical production and design of graphite rocket nozzles, missile heat shields, or nuclear moderating materials. This paper reports results from an investigation of the primary reaction kinetics of the carbon-oxygen reaction.

Reports from carbon-oxygen reaction studies date from the middle of the nineteenth century. Although some disagreement still exists, the conclusion that there is simultaneous liberation of carbon monoxide and carbon dioxide [first advanced by Rhead and Wheeler (*17*)] has gained wide acceptance. More recent work has shown this ratio to be an exponentially increasing function of temperature (*1*, *18*). Oxygen chemisorption and the formation of a surface complex appears to be prerequisite for reaction.

Recent development of sensitive analytical tools has enabled investigators to work at ever lower temperatures where results reflecting only the primary surface reactions can be obtained. Thus Gulbransen and Andrew (*8*) by suspending graphite from a precision microbalance were able to obtain measurable rates at 425°C. However product gas compositions were not obtained. Lewis, Gilliland, and Paxton (*16*) operated a graphite fluidized bed as low as 425°C. and obtained an essentially constant ratio of carbon monoxide to carbon dioxide up to the temperature where homogeneous carbon monoxide oxidation became important. Within the past year or two workers associated with the atomic energy establishments of England and France have studied nuclear graphite oxidation at temperatures approaching 400°C. (*13*, *14*, *15*).

Application of pore diffusion concepts developed from the field of heterogeneous catalysis has proved fruitful in reconciling discrepancies in kinetic data previously obtained. Here again low reaction rates (low temperatures) are necessary to avoid interference from diffusion effects within the porous solid. Wicke and his associates (*24*, *25*) have shown that above 500° to 600°C. pore diffusion influences must be considered important. Blyholder and Eyring (*3*), working at pressures less than 100 $\mu$, indicated that above 600°. graphite samples thicker than 0.1 mm. were affected by pore diffusion. Two recent literature surveys covering gas-carbon reactions in general are available (*2*, *22*). Extensive bibliographies are presented in both. Effron (*6*) has reviewed the literature particularly pertinent to the initiation mechanism.

## EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used during the experimental program and the procedures followed are described in detail elsewhere (*6*). The oxidation studies (except for one run to be discussed later) were carried out over ¼-in. diameter graphite rods. The reactor was stainless steel, 2-in. I.D., 5½ in. long, and ⅛ in. wall thickness. The reactor was placed at the end of a 1½-in. I.D. ceramic combustion tube packed with porcelain chips to serve as a preheater. The maximum temperature available in the preheater was 1,000°C. The graphite rods were placed in the reactor with their axes normal to the flow. An aluminum paint protected all surfaces from corrosion, and the system was thoroughly insulated. Gas samples were taken at the inlet and outlet of the reactor section. Standard devices regulated gas supply as needed.

Operating conditions used throughout the study were

$$2 < N_{Re} < 6$$

TABLE 1

| Run | Graphite type* | $a$,† sq. m./g. | Nominal grain size | $A_{carbon} \times 10^{-8}$, mg./min. sq. m. | $\sigma_c \times 10^{-8}$ | $A_{co} \times 10^{-8}$, cc./min. sq. m. | $\sigma_{co} \times 10^{-8}$ | $A_{co^2} \times 10^{-8}$, cc./min. sq. m. | $\sigma_{co2} \times 10^{-8}$ |
|---|---|---|---|---|---|---|---|---|---|
| GR 1 | AUC P7201 | 0.73 | 0.008 | 17.6 | 1.6 | 4.48 | 0.59 | 28.4 | 2.7 |
| GR 4 | AGKSP W16 | 0.42 | 0.019 | 11.2 | 1.7 | 2.17 | 0.031 | 17.3 | 3.3 |
| GR 5 | AGSR P2712 | 0.86 | 0.016 | 3.32 | 0.25 | 0.64 | 0.069 | 5.60 | 0.43 |
| GR 7 | AGKSP P19 | 0.86 | 0.019 | 7.89 | 0.68 | 1.73 | 0.28 | 13.1 | 0.95 |

* The designation of the graphites follows that of the supplier, that is the National Carbon Company. All graphites had a bulk density between 1.58 and 1.68 g./cc.

† Obtained from nitrogen adsorption by Dr. B. L. Harris, Glen Arm, Maryland.

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$$2.5 < v(\text{cm./sec.}) < 7.5$$

$$400 < T(^\circ\text{C.}) < 530$$

The Reynolds number was based on rod diameter. Artificial graphite was used throughout the study. The properties of this material are described in Table 1.

Reaction was followed by an analysis of the product gas with the system shown schematically in Figure 1. Again construction and operating details may be found elsewhere (6). Thermal conductivity was used as the basis for carbon dioxide analysis, whereas the carbon monoxide was determined by measuring the temperature rise resulting from its catalytic conversion to carbon dioxide in a hopcalite type of bed. The temperature rise was measured with a thermistor. A temperature rise of 0.0015°C. corresponded to 1 part/million carbon monoxide in oxygen.

Both the thermal conductivity cell and the carbon monoxide catalytic cell were immersed in a constant temperature oil bath controlled to ± 0.002°C. at approximately 20°C. The thermal conductivity cell was accurate to ± 10 parts/million carbon dioxide, and the conversion cell was able to detect changes in carbon monoxide concentration of 1 to 2 parts/million. Maximum carbon dioxide and carbon monoxide concentrations observed were 3,000 and 420 parts/million, respectively.

## RESULTS

### Introduction

Graphite samples were preheated in nitrogen to 525°C. at the beginning of each oxidation run. Subsequent heating, cooling, and all storage during down time was under nitrogen. Oxygen passed over the sample for at least 30 min. at the operating temperature before the product gas composition was measured. Blank determinations made with an empty reactor showed no significant background carbon dioxide or carbon monoxide concentration at any temperature employed.

Within a run graphite weight was computed from cumulative carbon monoxide and carbon dioxide concentrations. Samples were never oxidized to more than 20% weight loss in order to avoid graphite flaking under high burn-off conditions. Where necessary results were corrected for changes in graphite reactivity by normalizing the data to a standard activity. For this purpose standard temperature runs were interspersed with determinations at varying conditions. Increasing surface area of the sample with oxidation time is credited with causing these increased reactivities observed.

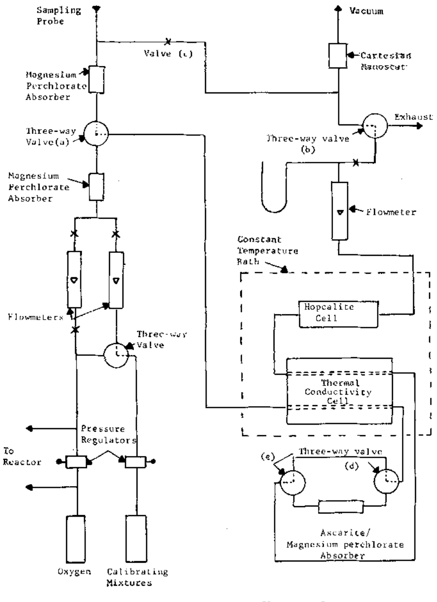

Fig. 1. Analytical system flow schematic.

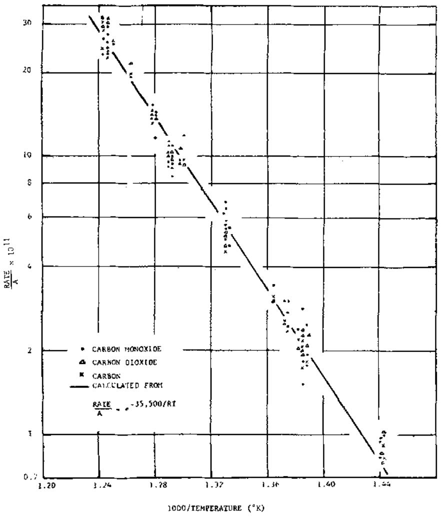

Fig. 2. Arrhenius plot.

Most determinations were carried out with oxygen or air flowing at 2.5 cm./sec. Some reseults were obtained at velocities of 5.0 and 7.5 cm./sec. to test the effect of gas velocity past the surface. Without exception graphite specimens removed from the reactor after oxidation exhibited a porous, spongelike appearance which to the naked eye was quite uniform throughout the rod. All data are available elsewhere (6). Summary and specimen data only are reported in this paper.

### Kinetic Results

All of the experimental data obtained during the project may be described with an equation of the form

$$\text{Rate} = A\,e^{-35{,}500/RT} \tag{1}$$

This result is shown in Figure 2. Table 1 lists values of $A$ for carbon burning, carbon monoxide production, and carbon dioxide production for the studies with pure oxygen at 2.5 cm./sec. linear flow rate over all four graphites used throughout the work. For each graphite type over twenty data points were used to obtain the value of $A$ listed. The values of $\sigma$ shown in the table indicate the goodness-of-fit of the final equations describing the results.

The rate of carbon combustion is expressed as *milligrams of carbon consumed per minute per square meter of BET surface.* The rate of carbon monoxide and carbon dioxide production is expressed as *STP cc of gas formed per minute per square meter of BET area.* The surface areas listed were obtained by nitrogen adsorption at 78°K. In these last measurements equilibration was found to be very rapid, and there was no difference between areas obtained from crushed specimens and those obtained from solid pieces. Hence the pore sizes must be large, interconnected, and accessible. Since the areas reported are low, the accuracy of these results cannot be more than approximately 10%.

Spectrographic analysis on the graphites was only partially successful owing to the low ash concentrations and the small size of sample saved for analysis. Nonetheless the spectrographic analysis yielded the following qualitative results:

GR 1—Graphite P 7201
  Largest amount of ash—principally silicon and aluminum oxides.
  Iron and chromium—none.
  Nickel—trace.
GR 4—Graphite W16
  No detectable ash.

TABLE 2. EFFECT OF VELOCITY ON REACTION RATE AT 520°C.

| Reynolds number | Carbon oxidation (mg./hr./g.) | Carbon dioxide-carbon monoxide ratio |
|---|---|---|
| 2.1 | 4.8 | 8.1 |
| 4.2 | 4.8 | 7.7 |
| 6.3 | 4.6 | 7.9 |

GR 5—Graphite P 2712
  Large amount of ash (less than GR 1).
  Ash principally silicon and iron oxides.
  No detectable alumina, chromium, nickel.
GR 7—Graphite P19
  Trace amounts of ash—traces of iron present.
  All other constituents below limit of detection.

### Effect of Velocity

The observed combustion rates and carbon dioxide–carbon monoxide ratios at velocities of 5 and 7.5 cm./sec. (twice and three times the base value used for all data summarized in Table 1) were found to agree with values predicted by Equation (1) with the value of A listed in Table 1 within the indicated value of $\sigma$ in all cases. Hence the carbon oxidation rate was independent of velocity as expected. Bulk oxygen diffusion is known to exert no influence on this process below approximately 800°C. (*20*). Table 2 lists typical results for the variation of the rate of oxidation and the carbon dioxide–carbon monoxide ratio at three different values of Reynolds number (based on graphite rod diameter). The conclusion must be that the observed oxidation was not influenced by flow rate past the rod surface.

### Carbon Dioxide-Carbon Monoxide Ratio

Surface reaction kinetics are obviously reflected in the relative amounts of carbon dioxide and carbon monoxide produced. Since activation energies for both carbon dioxide and carbon monoxide formation are found to be the same (for graphite rods under oxygen attack), it must be concluded that the carbon dioxide-carbon monoxide ratio is independent of temperature between 420° and 530°C.

In presenting rates of relative carbon dioxide-carbon monoxide formation the possibility of homogeneous after burning of carbon monoxide initially formed at the carbon surface must always be considered. The extent of homogeneous carbon monoxide oxidation may be estimated from a rate expression reported by Haslam (*9*):

$$r = k\left[P_{CO}{}^2 P_{O_2} - \frac{P_{CO_2}{}^2}{K}\right] \qquad (2)$$

For partial pressures in atmospheres (*10*)

$$\log k = 7.1899 - \frac{16{,}523}{T(°\text{R.})} \qquad (3)$$

For computational simplicity one can take the carbon monoxide partial pressure in the reactor to be the experimentally determined carbon dioxide concentration. This assumes that carbon monoxide is formed at the carbon surface, and all carbon dioxide is obtained by subsequent gas-phase oxidation. In addition the carbon monoxide concentration is assumed constant throughout the reactor, and gaseous decomposition of carbon dioxide is neglected. With these approximations, which are extreme, only 0.1% of the carbon monoxide present could be oxidized at 530°C. Therefore from both experimental results and a conservative calculation it is concluded that carbon dioxide and carbon monoxide concentrations measured between 420° and 530°C. reflect only surface reaction kinetics and are not influenced by gas-phase oxidation.

### Effect of Oxygen Concentration

The effect of oxygen concentration on reaction rate and activation energy was investigated with a spectroscopic graphite rod containing less than 6 parts/million ash and air instead of pure oxygen. Although the data are limited, the air oxidation results are directly comparable to those obtained with pure oxygen. Both activation energy and the carbon dioxide-carbon monoxide ratio were found to be unaffected by oxygen partial pressure. Constancy of this ratio is another indication of the lack of gas-phase carbon monoxide oxidation. If one assumes at low carbon dioxide and carbon monoxide concentrations that the rate may be expressed as

$$r = k\,P_{O_2}{}^n \qquad (4)$$

where $n$ is the reaction order, then an order of 0.60 is obtained between 420° and 530°C. Although this value was found from only two oxygen concentrations, hardly a basis from which to draw firm conclusions, it seems reasonable considering the available literature.

Walker et al. (*22*) noted that most data indicate the carbon-oxygen reaction to be first order or nearly first order. However if one restricts comparison to artificial graphite data, then this value of 0.60 is in better agreement with published results. Although Gulbransen and Andrew (*8*) reported the order to be nearly zero at pressures below 0.15-cm. mercury and first order above 10-cm. mercury, Blyholder and Eyring (*3*) note that the data are better represented by a half-order reaction over the entire range. With thin graphite wafers between 600° and 800°C. Blyholder and Eyring (*3*) also observed half-order kinetics. They reported zero-order kinetics with graphite coated on a ceramic support and hence claimed a strong influence of pore diffusion in their studies with the thin wafers. However the influence of their ceramic support on the graphite oxidation has not been defined. Their studies may have encompassed two different mechanisms since their results of 80,000 cal./g. mole and zero order for graphite coated on ceramic rods agree with no other published data.

### Effect of Diffusion within the Sample Pores

Oxygen transport to reaction sites within the porous graphite is known to influence oxidation rates. The Weisz criterion (*23*) for the relative importance of diffusive effects in heterogeneous catalysis makes use of the experimentally observed reaction rate rather than the specific rate constant, since the latter is not explicitly known. This criterion is applicable here. However direct application to experimental combustion rates is not usually possible since $D_{\text{eff}}$ is not explicitly known. Actual diffusivities may deviate appreciably from calculated values. The best method of applying the Weisz criterion to the present data is to determine $D_{\text{eff}}$ from literature results covering a sufficiently wide temperature range to clearly indicate where diffusive inhibition begins. The value of $D_{\text{eff}}$ calculated at that temperature where the Arrhenius curve first deviates from a straight line is compared with that $D_{\text{eff}}$ required to cause diffusive inhibition in the data being considered. Two investigations from which such a comparison can be drawn are available. Application of the Weisz criterion to Rossberg and Wicke's (*19*) data at 600°C. yields a $D_{\text{eff}}$ of $2 \times 10^{-2}$ to $2 \times 10^{-3}$ sq. cm./sec. depending on the assumption of first- or zero-order kinetics. Walker's data (*22*) for the Boudouard reaction under 1 atm. pressure indicated no pore diffusion effects below 975°C. Calculation of $D_{\text{eff}}$ for carbon dioxide at this temperature and extrapolation to oxygen at 530°C. yields a $D_{\text{eff}}$ of about $10^{-3}$ sq. cm./sec. In this article Walker also reported an experimentally determined $D_{\text{eff}}$ for carbon dioxide through product carbon monoxide within the pore structure of unreacted spectroscopic carbon of $10^{-2}$ sq. cm./sec.

TABLE 3. EFFECT OF PARTICLE SIZE ON THE CARBON DIOXIDE-CARBON MONOXIDE RATIO*

| | Carbon dioxide-carbon monoxide ratio<br>Oxygen | <br>Air |
|---|---|---|
| ¼-in. rod (lot W16) | 8.2 | 8.3 |
| 0.015-in. wafers (lot 19P) | 6.1 | 4.4 |

* With AKGSP graphite.

With the assumption of half-order kinetics for the 530°C. —¼-in. graphite rod data obtained from this present study the Weisz criterion would require a $D_{\text{eff}}$ of less than $10^{-4}$ sq. cm./sec. for pore diffusion to be of importance. The same comparison can be made for the data of Gulbransen and Andrew (*8*), who reported a similar activation energy. At 575°C. a $D_{\text{eff}}$ less than $10^{-5}$ sq. cm./sec. would have been necessary for their data to have been influenced by diffusive effects. From the low values of these calculated diffusivities it is probable that the present carbon burn-off data are not influenced to a significant degree by diffusive effects.

To test the effect of sample particle size studies were made over the same temperature range with 0.015-in. wafers cut from the ¼-in. graphite rods. The energy of activation was found to be approximately 5 kcal./mole higher than for rod oxidation. The higher wafer activation energies indicate that pore diffusion may begin to influence the complete utilization of ¼-in. graphite rods above 500°C. The wafers would require a $D_{\text{eff}}$ of $3 \times 10^{-6}$ sq. cm./sec. at 530°C. (300 times less than that of the rod) before encountering diffusive inhibition.

The reaction order obtained with ¼-in. rods was found to be 0.60. That found for the wafers was 0.68 indicating a possible effect of particle size. However the significance of this difference is not certain. The particle size does have an important influence on the carbon dioxide-carbon monoxide ratio. This is shown in Table 3. The importance of particle size on oxidation products might well explain some of the conflicting literature results.

If a sequential mechanism of the form $C \rightarrow CO \rightarrow CO_2$ is assumed, as proposed in the following section, then the relative amounts of oxide products formed should vary with particle size. In a larger particle carbon monoxide first formed would have a longer residence time in the sample pore structure and hence a greater chance for further reaction. (Alternatively the mean carbon monoxide concentration within the larger particle would be higher.) An example of such successive reactions in carbon combustion was reported by Weisz (*23*). He observed the carbon dioxide-carbon monoxide ratio differed from the primary ratio produced at the reaction site because of further catalyzed reaction ($CO \rightarrow CO_2$) during diffusive passage of the carbon monoxide molecules out of a particle.

## MECHANISM AND KINETICS

Any proposed kinetic mechanism should reconcile the following experimental results:

1. The reaction order with respect to oxygen is found to be between half and first-order.
2. The carbon dioxide-carbon monoxide ratio is found to be independent of temperature (even though the equilibrium constant for this system changes a hundredfold over the same temperature range).
3. The carbon dioxide-carbon monoxide ratio is found to depend on oxygen partial pressure (at least for thin graphite specimens).
4. The carbon dioxide-carbon monoxide ratio is found to depend on particle size.

One mechanism which satisfactorily explains these observations is described below.

Step 1. Formation of the surface complex. The surface complex is taken to be formed in two steps. Experiments with isotopic oxygen mixtures have indicated that oxygen atoms in the carbon dioxide molecule do not originate from the same oxygen molecule (*21*). Hence oxygen dissociation or weakening of the oxygen molecule bond, an assumed reversible reaction always near equilibrium on the surface, occurs first. The surface complex then may form from reaction between carbon and adsorbed oxygen atoms. The rate of formation of the surface complex $r_1$ may be expressed as

$$r_1 = k_1 P_{O_2}{}^{1/2} \tag{5}$$

Step 2. Breakup of the surface complex to carbon monoxide. Such a primary step is required since at 500°C. a larger carbon monoxide-carbon dioxide ratio was experimentally detected than could have resulted from reaction between carbon dioxide (on the assumption it was the only primary product) and graphite. With negligible back reaction (since carbon monoxide is not adsorbed by graphite at these temperatures) the rate of formation of carbon monoxide from this reaction is

$$r_2 = k_2\,\theta \tag{6}$$

where $\theta$ is the fraction of the graphite surface covered by oxide complex.

Step 3. Breakup of the surface complex to carbon dioxide. This reaction is also taken as unidirectional since carbon dioxide adsorption below 1,000°C. has been found to proceed without a pressure decrease (*5*), and transfer of carbon-14 from tagged carbon dioxide has been found to be negligible (*4*). The rate of complex breakup to carbon dioxide $r_3$ may thus be written as

$$r_3 = k_3\,\theta^2 \tag{7}$$

Step 4. Oxygen transfer between surface complex and gaseous carbon monoxide:

$$[\text{surface complex}] + (CO)_g \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CO_2)_g + C$$

This is a reversible reaction favoring carbon dioxide below 600° to 700°C. (*7*). Such an oxygen transfer explains the observations of Lambert (*11, 12*) and Rhead and Wheeler (*17*) on the rapid oxidation of carbon monoxide over carbon surfaces as low as 300°C. The reverse of this reaction is widely postulated as the initial step of the Boudouard reaction. The rate of this transfer $r_4$ is

$$r_4 = k_4\,\theta P_{CO} - k_{-4}\,P_{CO_2}(1 - \theta) \tag{8}$$

At steady state

$$r_1 = r_2 + r_3 + r_4 \tag{9}$$

Hence

$$\theta = \frac{k_1\,P_{O_2}{}^{1/2} + k_{-4}\,P_{CO_2}}{k_2 + k_4\,P_{CO} + k_{-4}\,P_{CO_2} + k_3\,\theta} \tag{10}$$

under the conditions of low surface coverage by the complex, large $k_2$, low carbon monoxide and carbon dioxide concentrations, little oxide formation by carbon dioxide. This may be simplified to

$$\theta \approx \frac{k_1}{k_2} P_{O_2}{}^{1/2} \tag{11}$$

The rate of carbon monoxide formation $r_{co}$ is $r_2 - r_4$; hence

$$r_{co} \approx k_1\,P_{O_2}{}^{1/2} \tag{12}$$

and $r_{co_2}$ the rate of carbon dioxide formation is $r_3 + r_4$, or

$$r_{co_2} \approx \frac{k_1^2\, k_3}{k_2^2} P_{O_2} + \frac{k_1\, k_4}{k_2} P_{O_2}^{1/2}\, P_{co} \tag{13}$$

Carbon combustion $r_c$ equals the sum of $r_{co}$ and $r_{co_2}$, or

$$r_c \approx \frac{k_1^2\, k_3}{k_2^2} P_{O_2} + k_1\, P_{O_2}^{1/2} \left[ 1 + \frac{k_4\, P_{co}}{k_2} \right] \tag{14}$$

and the carbon dioxide-carbon monoxide ratio $r_{co_2}/r_{co}$ is

$$\frac{r_{co_2}}{r_{co}} \approx \frac{k_1\, k_3}{k_2^2} P_{O_2}^{1/2} + \frac{k_4}{k_2} P_{co} \tag{15}$$

Equation (14) predicts a reaction order between half and first depending on the relative magnitudes of the individual rate constants. The relative rate of complex breakup to gaseous products determines which limit is approached. Literature results indicating first- or near first-order reaction, and more particularly orders of 0.60 and 0.68 obtained in this study, are consistent with Equation (14).

Results for the thin graphite disks (Table 3) are in accord with Equation (15) in that the carbon dioxide-carbon monoxide ratio decreases with decreasing oxygen partial pressure. Lewis et al. (*16*) also observed this at oxygen partial pressures below 0.1 atm. That such a trend is not evident for the ¼-in. graphite rods is due to the greater probability of carbon monoxide conversion (Step 4) during its relatively long diffusive passage out of the particle. The large particle not only masks the oxygen partial pressure functionality but also yields relatively more carbon dioxide during both air and oxygen reaction. Lambert (*11, 12*) too found that longer beds (that is greater contact time) produced relatively more carbon dioxide.

The temperature dependence of the carbon dioxide-carbon monoxide ratio is predicted by Equation (15) to depend on the ratio $k_1k_3/k_2^2$ (with the assumption that the $P_{co}$ term is relatively small). If the sum of the activation energies of $k_1$ and $k_3$ is approximately equal to twice that of $k_2$, then $r_{co_2}/r_{co}$ would be independent of temperature as found experimentally during this study.

## CONCLUSIONS

Graphite oxidation between 420° to 530°C. has been found to yield a reaction order between ½ and 1, and an activation energy of 35 to 40 kcal/g. mole. With ¼-in. rods used, kinetic data were only slightly influenced by diffusive effects at the upper temperature limit.

Particle size has been shown to have an important influence on the relative amounts of carbon dioxide and carbon monoxide produced.

A reaction mechanism has been proposed which explains the present data and the bulk of literature results obtained below 600°C. The mechanism postulates the *primary formation* of carbon monoxide and carbon dioxide at the graphite surface followed by oxygen exchange between the desorbed carbon monoxide molecule with the surface complex to yield additional carbon dioxide.

## ACKNOWLEDGMENT

This project was supported in part by funds from the National Science Foundation and in the initial phases by a grant from the National Aeronautics and Space Administration. The authors gratefully acknowledge this assistance.

Thanks are due the National Carbon Company, a division of Union Carbide Corporation, for its donations of graphite samples, to the Mine Safety Appliance Company for its endeavors in producing a low temperature catalytic oxidation bed, and to the Linde Company, a division of Union Carbide Corporation, for a supply of molecular sieve.

During the first three years of study one of the authors (Effron) held the Allied Chemical Fellowship, and he wishes to express his appreciation for this assistance.

Mr. Bernard Baker was largely responsible for construction of the equipment used throughout the project. The authors particularly wish to extend a note of appreciation for this contribution to the success of the work done. Dr. Paul Emmett reviewed the manuscript at an early stage in its development. The authors are grateful for his assistance.

## NOTATION

$a$ = BET surface area, sq. m./g.
$A$ = Arrhenius constant
$d_R$ = rod diameter
$G$ = mass velocity
$k$ = rate constant
$K$ = equilibrium constant
$N_{Re}$ = Reynolds number = $d_RG/\mu$
$n$ = order in rate equation
$P$ = partial pressure
$r$ = rate
$T$ = temperature
$\theta$ = fraction of surface area
$\sigma$ = standard deviation
$\mu$ = gas viscosity

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*Manuscript received April 9, 1963; revision received October 28, 1963; paper accepted October 30, 1963.*