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# Fundamental Aspects of the Reaction of Oxygen With Carbon Adsorbents<sup>1</sup>

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The kinetics for the oxidation of the carbon in a coconut-shell charcoal, a new bone char, two service bone chars, and a spent bone char was found to be retarded first-order in character. The experimental data were obtained in a flow system with nitrogen-oxygen gas mixtures at temperatures below 400° C. Using the initial fractional rate of oxidation of the carbon as the criterion of evaluation, a linear plot against oxygen concentration was obtained for each temperature at which the combustion was studied. The influence of temperature was expressed as the sum of two exponential Arrhenius-type terms. A single relationship was derived by combining the effects of these two variables. This relationship proved equally valid when applied to all carbon adsorbents investigated. Some reaction mechanisms were proposed that were consistent with the experimental findings of the investigation.

## I. Introduction

The study of the kinetics of combustion of carbon was initiated about 85 yr ago [1, 2],<sup>3</sup> and it was early appreciated that the subject was highly complex. Oxygen was found to react with carbon at temperatures much lower than those associated with ordinary burning, and the reaction was explained by the postulation of the formation of stable surface complexes. Rhead and Wheeler [3] in 1912 to 1913 found that it was not possible to break down these complexes by evacuating at the same temperatures at which they were formed. McLean [4] confirmed these findings years later and observed that above 200° C none of the oxygen is recovered in the uncombined state. Later, different forms of surface oxide complexes were suggested to explain the results of measurements of heats of adsorption of oxygen on a charcoal. Very high values were identified with the initial

uptake of oxygen, and these values dropped off rapidly with the addition of more oxygen [5, 6].

In 1932 Kolthoff [7] demonstrated the existence of different specific oxide complexes on charcoals by observing either predominantly acidic or basic properties, depending upon the conditions under which the sample had been heated. A few years later Klemenc, Wechsberg, and Wagner [8] proposed carbon suboxide (C<sub>3</sub>O<sub>2</sub>) as the intermediate complex formed during the combustion of carbon. They pointed out that the ratio of carbon dioxide to carbon monoxide, which could be predicted from the decomposition of carbon suboxide at 400° C, was of the same magnitude as that observed in the combustion of carbon at that temperature. Rhead and Wheeler [3] believed the oxide complex to have a variable composition C<sub>x</sub>O<sub>y</sub>, with *x* and *y* having different values, depending upon the temperature so as to break down into carbon monoxide and carbon dioxide in varying relative amounts. This view was shared by Haslam [9], Shah [10], and also Oshima [11].

Chukhanov and Karzhavina [12] believed that the intermediate complex existed in the form C<sub>3</sub>O<sub>4</sub>, which might decompose directly or combine with more carbon and oxygen so as to yield

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<sup>3</sup> Figures in brackets indicate the literature references at the end of this paper.

different relative amounts of carbon dioxide and carbon monoxide. Strickland-Constable [13] cited data supporting the simultaneous existence of two types of surface oxide, to which he assigned the names "Labile" and "Stable".

The apparent order of the oxidation reaction has also been subjected to considerable study. The results have varied, depending upon the source and history of the type of carbon studied, the temperature, pressures, oxygen concentration, and in some cases upon the rate of flow of the reactant gases. A wide range of activation energies also have been reported in the literature. Values as high as 100,000 [14] and as low as 20,000 [15] calories have been obtained in the same temperature range and for similar types of carbon. Mayer [16] in a review article in 1934 concluded that no complete formulation of the rates or mechanism of the combustion of carbon was yet possible.

In spite of the variety of experimental methods employed, most of the recorded investigations agree on one of several important factors: the relative quantity of gaseous carbon dioxide compared to carbon monoxide increases with the time of contact of the reactant gases with the carbon sample. This effect was noted by Meyer [17] in the oxidation of a carbon filament at high-flow velocities; by Lambert [18] using a granular bed of charcoal; and by Tsukhanova [19] during the passage of air through a hollow carbon cylinder. Recently, the effect was observed by Deitz [20] in a plant-scale oxidation of bone char by passage through a rotary decarbonizer. Samples of gas were collected from various positions within the decarbonizer for analysis. The ratio of carbon dioxide to carbon monoxide increased to as high as 40:1 as the gases moved from the hotter region toward the cooler end from which they were withdrawn. These examples point to a possible secondary oxidation of the carbon monoxide that is formed as one of the primary products during the combustion.

## II. Status of Present Investigation

In a previous article [22] the rate of combustion of bone char and other carbon adsorbents was followed with respect to carbon. The data for bone char satisfied the requirements of a retarded first-order reaction. The equation, in its integrated

form, which lent itself most readily to a direct evaluation of the reaction rate constant was stated as follows:

$$\frac{1}{t} \ln \left[ \frac{1}{1-f} \right] = k - b \frac{1}{t} \left[ \left( \ln \frac{1}{1-f} \right) - f \right], \quad (1)$$

where

- $t$  = time (hours) measured from steady-state conditions;
- $f$  = fraction of the original carbon present in the sample that had burned in  $t$  hours;
- $k$  = reaction-rate constant (reciprocal hours);
- $b$  = a constant whose numerical value is related to the extent of retardation.

The reaction-rate constant was determined for one bone char (char 2) at different oxygen concentrations, but at the same temperature and flow rate. Under these conditions it was found that a plot of  $k$  against percentage of oxygen gave a straight line. This line, when extrapolated to zero percent of oxygen, intercepted the  $k$  axis at a value greater than zero. The same situation was found to exist for an activated carbon (char 6) where the retardation was so slight that a simple (unretarded) first-order relationship fitted the data satisfactorily. When  $\ln k$  was plotted against  $1/T$  for a new bone char, the resultant graph deviated markedly from linearity.

In the present paper a more detailed study is presented of the effects of oxygen concentration and temperature for a coconut-shell charcoal (char 1) and number of different bone chars. Plausible mechanisms are suggested for the combustion process that are consistent with the observed dependence of the initial reaction rate upon these variables.

## III. Procedure

The apparatus and procedure have been described earlier [22]. Oxygen-nitrogen mixtures of known composition were passed downward through a vertically supported reaction tube containing the sample. The reaction products were then determined gravimetrically. The temperature, oxygen concentration, and rate of flow were held constant for a given combustion experiment; and the resultant carbon dioxide and carbon monoxide were measured at known intervals of time. The amount of carbon burned during each time inter-

val was computed from these quantities and expressed as a fraction of the total carbon originally present in the sample. In every case, measurements were corrected to steady-state conditions. Equation 1 was employed for the evaluation of the rate constant  $k$  by plotting the function

$$\frac{1}{t} \ln \left[ \frac{1}{1-f} \right],$$

against

$$\frac{1}{t} \left[ \ln \left( \frac{1}{1-f} \right) - f \right],$$

and determining the intercept of the resultant straight line.

#### IV. Independence of $k$ and Dependence of $\text{CO}_2/\text{CO}$ Upon Sample Weight

Several combustion experiments were conducted with new bone char (char 2) at 280° C, 4.8-percent oxygen in nitrogen and three separate flow rates: 270, 330, and 465 ml/min. The samples varied in weight from about 0.5 to 6.0 g. The results are listed in table 1 in the order of increasing weight of sample within a group of a given flowrate. A comparison of the second and fifth columns shows no dependence of rate constant upon sample weight at a flowrate of either 270 or 465 ml/min. An examination of the fifth column discloses only a slight effect of flow-rate upon  $k$ .

TABLE 1. Comparison of the rate constants and the ratios  $\text{CO}_2/\text{CO}$  with sample weights for char 2 (a new bone char) at three different rates of flow

All measurements were made at 280° C and 4.8 percent oxygen in nitrogen

Experiment	Weight of sample (W)	Flow rate (V)	$\text{CO}_2/\text{CO}$	Rate constant (k)
	g	ml/min		1/hr
15.....	0.484	270	2.1	0.126
18.....	.601	270	2.7	.094
17.....	.727	270	2.5	.101
16.....	.972	270	4.1	.118
21.....	.987	330	3.3	.080
13.....	.485	465	1.4	.18 (?)
14.....	.730	465	1.9	.087
12.....	.986	465	2.6	.084
3.....	.988	465	2.6	.090
11.....	1.936	465	4.0	.102
1.....	1.996	465	3.3	.063 (?)
20.....	3.392	465	5.5	.091
4.....	4.824	465	6.5	.091
2.....	4.983	465	6.2	.081
19.....	5.856	465	6.1	.096

It may be seen from the fourth column of table 1 that the ratio of carbon dioxide to carbon monoxide definitely increases with increasing weight of sample within each group of flow rates.<sup>4</sup> Furthermore, higher ratios are seen to be associated with lower flow rates. This is demonstrated by comparing the ratio of carbon dioxide to carbon monoxide for experiments 16, 21, 12, and 3, all of which are based on sample weights close to 1 g. These ratios at 270, 330, and 465 ml/min are 4.1, 3.3, and 2.6, respectively. Moreover, when each of the ratios mentioned is multiplied by the corresponding flow rate, the values 1,100, 1,100, and 1,200, respectively, are obtained. Since velocity of flow is inversely proportional to the time of contact, this demonstrates clearly that for the same weight of sample the  $\text{CO}_2/\text{CO}$  ratio is directly proportional to the time of contact of the reaction mixture with the char sample.

#### V. Influence of Oxygen Concentration and Temperature on the Reaction Rate Constant

Equation 1 is the integrated form of the equation:

$$\frac{df}{dt} = k \frac{1-f}{1+bf}, \quad (2)$$

where both  $k$  and  $b$  may be considered to be functions of oxygen concentration and temperature, and  $df/dt$  is the fractional rate of combustion of the carbon in the sample. It may be seen from eq 2 that  $k$  is the limiting value of  $df/dt$  as  $t$  tends toward zero. An alternative definition of  $k$  is, therefore, the initial rate of combustion. A plot of  $k$  against mole fraction of oxygen is given in figure 1 for a coconut-shell charcoal (char 1) at a flow of 270 ml/min at the indicated temperatures. The values of  $k$  were obtained from the experimental data by use of eq 1. These values are given in columns 3 and 5 of table 2.

The results for a new bone char, 2; service char, 35; service char, 3; and spent char, 27 also gave linear dependences of  $k$  upon oxygen concentration, as may be seen from the unbroken lines in

<sup>4</sup> It is felt that the tapering off of the last two figures in column 4 (i. e., 6.2 and 6.1) is not a real effect. It is possible that the capacity of the carbon dioxide absorption tube in the analysis train was slightly exceeded when the highest weight samples were used. This would have allowed a small amount of  $\text{CO}_2$  to pass through and be included later with the  $\text{CO}$ .

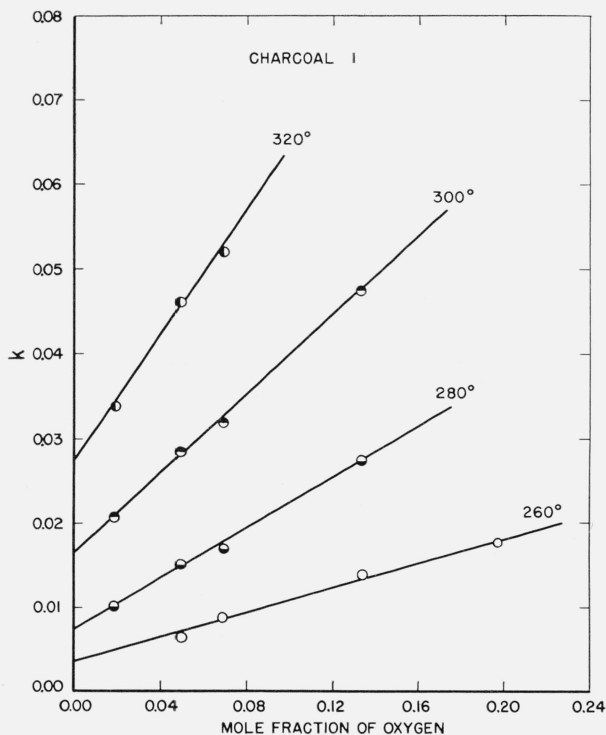


FIGURE 1. Rate constant  $k$  as a function of oxygen concentration for char 1 (a coconut-shell charcoal) at 260°, 280°, 300°, and 320° C and a flow rate of 270 ml/min (see also table 2).

TABLE 2. Rate constants for the combustion of char 1 (a coconut-shell charcoal) at a flow rate of 270 ml/min for various percentages of oxygen in nitrogen and at the four temperatures indicated (see also fig. 1)

Experiment	Temperature	Oxygen	Weight of sample	$k$ (observed)
	° C.	Percent	g	1/hr
141.....	260	4.92	0.6477	0.0064
139.....	260	6.93	.8365	.0089
140.....	260	13.29	.3915	.0158
142.....	260	19.71	.2939	.0176
133.....	280	1.83	.4742	.0102
134.....	280	4.92	.5820	.0151
131.....	280	6.93	.5231	.019
132.....	280	13.29	.3744	.0275
128.....	300	1.83	.5300	.0206
130.....	300	4.92	.4912	.029
126.....	300	6.93	1.2025	.032
129.....	300	13.29	.3779	.0475
137.....	320	1.83	.3204	.0337
138.....	320	4.92	.5293	.0474
135.....	320	6.93	.4995	.062

figures 2, 3, 4, and 5. The values are given in columns 3 and 5 of tables 3, 4, 5, and 6, respectively.

TABLE 3. Rate constants for the combustion of char 2 (a new bone char) at a flow rate of 270 ml/min for various percentages of oxygen in nitrogen and at the four temperatures indicated

The figures in the last column were calculated from equations of the broken lines shown in figure 2

Experiment	Temperature	Oxygen	Weight of sample	$k$ (observed)	$k$ (calculated)
	° C	Percent	g	1/hr	1/hr
111.....	260	1.83	1.9686	0.058	.....
112.....	260	4.92	1.9435	.0698	.....
68.....	260	11.3	1.1963	.086	.....
73.....	260	11.3	1.3264	.089	.....
110.....	260	20.56	1.9388	.117	.....
109.....	280	1.83	1.9527	.080	.....
15.....	280	4.8	0.4835	.101	.....
18.....	280	4.8	.6007	.094	.....
17.....	280	4.8	.7268	.101	.....
16.....	280	4.8	.9716	.104	.....
107.....	280	6.93	1.9487	.116	.....
103.....	280	6.93	1.9632	.112	.....
23.....	280	11.3	0.7339	.145	.....
69.....	280	11.3	1.1996	.115	.....
70.....	300	11.3	1.0874	.27	0.25
72.....	300	11.3	1.0961	.25	.25
65.....	320	1.9	2.4335	.203	.16

It is immediately evident from figure 1 that  $k$  exhibits a linear dependence upon the mole fraction of oxygen, regardless of the temperature at which the combustion was carried out. An extrapolation to zero mole fraction yields a positive intercept greater than zero on the  $k$  axis. Both the intercept,  $I_T$ , and the slope,  $S_T$ , increase as the temperature increases. The initial rate of combustion may then be written in the form

$$k = I_T + [O_2]S_T, \quad (3)$$

where  $[O_2]$  is the mole fraction of oxygen,  $I_T$  and  $S_T$  being functions of the temperature and independent of one another.

The numerical values of  $I_T$  and  $S_T$  may be computed graphically from the data of table 2 and figure 1 corresponding to each of the four temperatures indicated. If, now,  $\ln I_T$  and  $\ln S_T$  are each plotted against the reciprocal of the absolute

TABLE 4. Rate constants for the combustion of char 35 (a service bone char) at a flow rate of 270 ml/min for various percentages of oxygen in nitrogen and at the six temperatures indicated

The figures in the last column were calculated from equations of the broken lines shown in figure 3

Experiment	Temperature	Oxygen	Weight of sample	k (observed)	k (calculated)
	$^{\circ}C$	Percent	g	1/hr	1/hr
92.....	280	1.83	2.4917	0.0136	-----
60.....	280	1.9	2.4807	.0141	-----
62.....	280	1.9	2.4861	.0142	-----
89.....	280	4.92	1.9868	.0192	-----
99.....	280	4.92	2.0076	.0194	-----
91.....	280	4.92	2.4996	.0195	-----
88.....	280	6.93	1.9882	.021	-----
87.....	280	6.93	2.4773	.018	-----
93.....	280	6.93	2.5009	.022	-----
97.....	280	13.29	2.0075	.027	-----
96.....	280	13.29	2.4752	.027	-----
100.....	280	19.71	2.0211	.031	-----
98.....	280	19.71	2.4875	.033	-----
95.....	280	20.56	1.9885	.036	-----
94.....	280	20.56	2.4978	.032	-----
59.....	300	1.9	2.4876	.027	0.030
63.....	300	1.9	2.4888	.029	.030
54.....	320	1.9	2.4896	.066	-----
117.....	320	4.92	1.9909	.095	-----
118.....	320	6.93	2.0131	.1345	-----
55.....	340	1.9	2.4946	.16	.16
56.....	360	1.9	1.3501	.46	.35
64.....	360	1.9	2.4878	.42	.35
57.....	380	1.9	1.1457	.88	.88

TABLE 5. Rate constants for the combustion of char 3 (a service bone char) at a flow rate of 270 ml/min for various percentages of oxygen in nitrogen and at the five temperatures indicated

The figures in the last column were calculated from equations of the broken lines shown in figure 4

Experiment	Temperature	Oxygen	Weight of sample	k (observed)	k (calculated)
	$^{\circ}C$	Percent	g	1/hr	1/hr
27.....	260	4.8	1.4969	0.018	0.015
26.....	260	4.8	2.4873	.018	.015
121.....	280	1.83	2.0562	.023	-----
24.....	280	4.8	1.9994	.035	-----
25.....	280	4.8	2.9852	.036	-----
119.....	280	13.29	1.9878	.058	-----
31.....	300	4.8	.7477	.085	.081
30.....	300	4.8	1.4948	.069	.081
124.....	320	1.83	2.0174	.100	-----
33.....	320	4.8	1.4911	.193	-----
32.....	320	4.8	2.4848	.194	-----
123.....	320	6.93	2.0085	.23	-----
34.....	340	4.8	1.0024	.44	.44

TABLE 6. Rate constants for the combustion of char 27 (a spent bone char) at a flow rate of 270 ml/min for various percentages of oxygen in nitrogen and at the five temperatures indicated

The figures in the last column were calculated from equations of the broken lines shown in figure 5

Experiment	Temperature	Oxygen	Weight of sample	k (observed)	k (calculated)
	$^{\circ}C$	Percent	g	1/hr	1/hr
47	280	1.9	2.4903	0.042	-----
104	280	6.93	1.9973	.071	-----
105	280	13.29	1.9984	.089	-----
106	280	20.56	1.9941	.127	-----
48	300	1.9	2.2428	.089	0.086
49	320	1.9	0.9965	.173	-----
44	320	1.9	2.4934	.157	-----
114	320	6.93	1.9989	.227	-----
108	320	13.29	1.9965	.43	-----
116	320	19.71	1.9898	.44	-----
113	320	20.56	2.0073	.445	-----
42	340	1.9	0.9979	.38	.31
43	340	1.9	1.4948	.34	.31
38	360	1.9	1.0575	.77	.56
39	360	1.9	1.4850	.70	.56

temperature, a linear relationship is obtained in both cases, as is borne out by figure 6.

$$I_T = Ae^{-\frac{E_1}{RT}}, \quad (4)$$

and

$$S_T = Be^{-\frac{E_2}{RT}}, \quad (5)$$

where the constants  $A$ ,  $E_1$ ,  $B$ , and  $E_2$  may be evaluated from the linear plots of figure 6. Upon substitution of eq 4 and 5 in eq 3, the dependency of  $k$  upon temperature as well as oxygen concentration is obtained as given in eq 6:

$$k = Ae^{-\frac{E_1}{RT}} + B[O_2]e^{-\frac{E_2}{RT}}, \quad (6)$$

A test of the experimental validity of eq 6 was next applied to the other carbonaceous adsorbents (i. e., bone chars) studied in this investigation. A similar treatment was made only for those data that show no entries in the last column in tables 3, 4, 5, and 6. This corresponds to the two unbroken lines in each of the figures 2, 3, 4, and 5.<sup>5</sup>

A numerical evaluation of the four parameters of eq 6 was thus obtained for each of the four bone chars, since only two lines are necessary for this

<sup>5</sup> These particular choices were made when three or more points were available for determination of the unbroken lines.

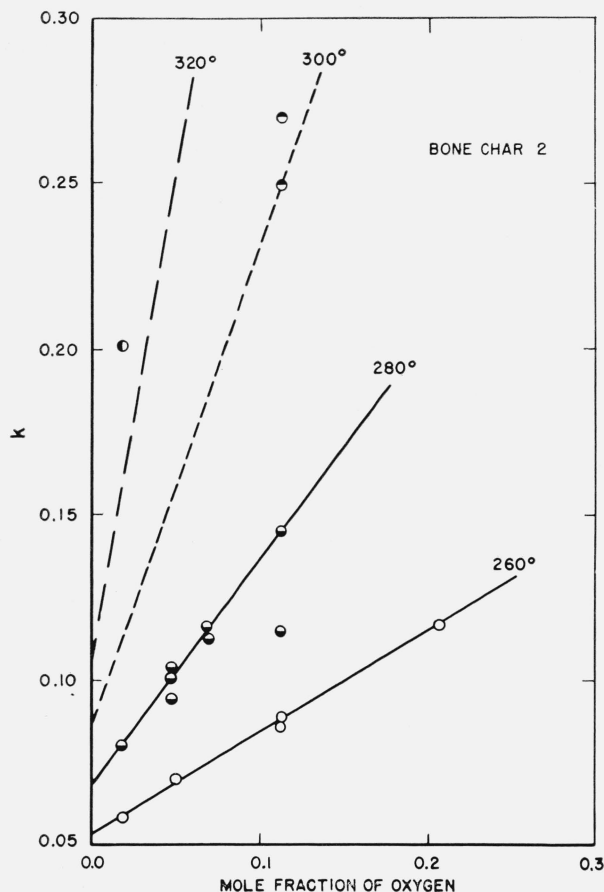


FIGURE 2. Rate constant  $k$  as a function of oxygen concentration for char 2 (a new bone char) at 260°, 280°, 300°, and 320° C and a flow rate of 270 ml/min.

The broken lines were constructed by using eq 6 with appropriate parameters computed from equations of the continuous lines at 260° and 280° C. (See also table 3.) The continuous lines are drawn through experimental points.

type of determination. The broken lines in figures 2, 3, 4, and 5 were then constructed from eq 6 by using values of  $T$  at which other measurements had been made. The closeness of fit of these points with the predicted lines so constructed is evidenced from an examination of the figures. A numerical comparison of observed and calculated values of  $k$  is available between the last two columns of tables 3, 4, 5, and 6. The numerical values of the parameters  $A$ ,  $B$ ,  $E_1$ , and  $E_2$  for each of the materials investigated in this paper are given in table 7.

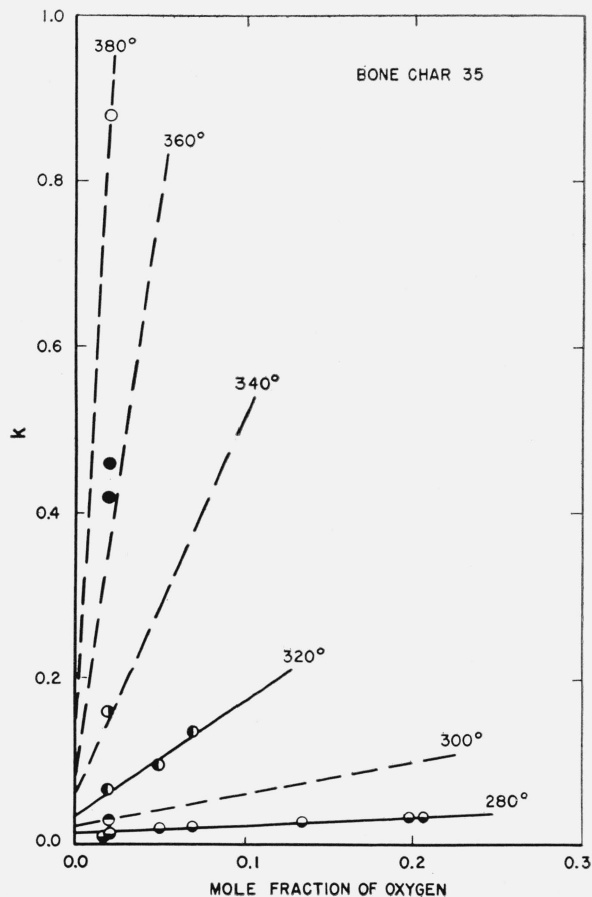


FIGURE 3. Rate constant  $k$  as a function of oxygen concentration for char 35 (a service bone char) at 280°, 300°, 320°, 340°, 360°, and 380° C and a flow rate of 270 ml/min.

The broken lines were constructed by using eq 6 with appropriate parameters computed from equations of the continuous lines at 280° and 320° C. (See also table 4.) The continuous lines are drawn through experimental points.

## VI. Theoretical Considerations

Any mechanism, in addition to predicting the observed results, must be consistent with accepted thermodynamic concepts. To be of real value the mechanism should predict unknown facts concerning the reaction and thus point the way for further investigations.

One reaction that is known to take place in connection with the combustion of solid carbonaceous adsorbents is the catalytic oxidation of CO to form CO<sub>2</sub>. Evidence in support of this may be gained from the data contained in table 1 by

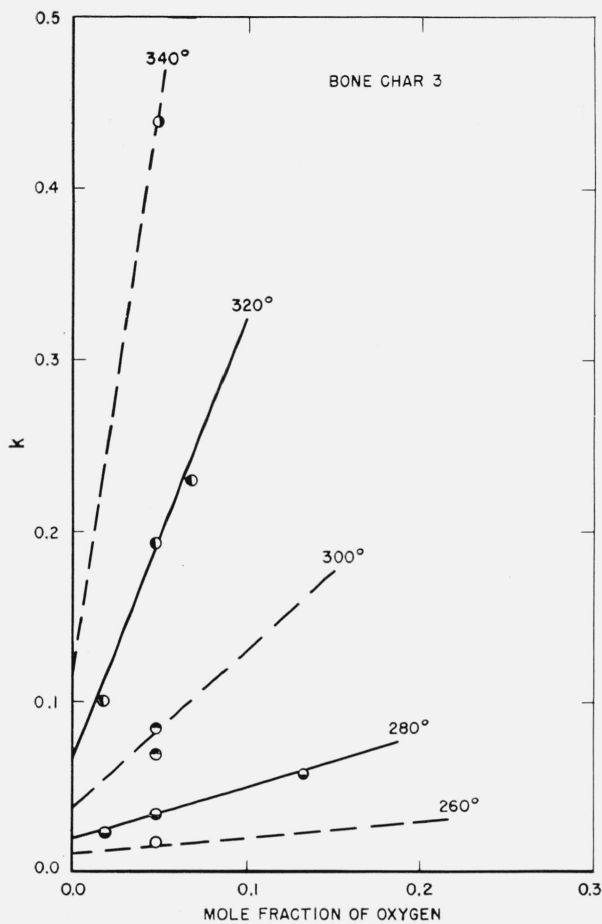


FIGURE 4. Rate constant  $k$  as a function of oxygen concentration for char 3 (a service bone char) at 260°, 280°, 300°, 320°, and 340° C and a flow rate of 270 ml/min.

The broken lines were constructed by using eq 6 with appropriate parameters computed from equations of the continuous lines at 280° and 320° C. (See also table 5.) The continuous lines are drawn through experimental points.

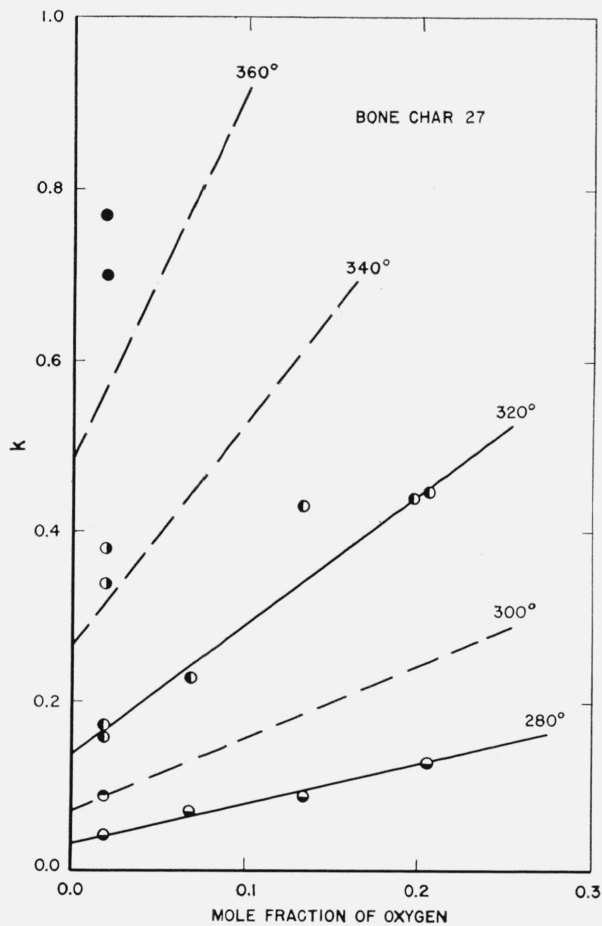


FIGURE 5. Rate constant  $k$  as a function of oxygen concentration for char 27 (a spent bone char) at 280°, 300°, 320°, 340°, and 360° C and a flow rate of 270 ml/min.

The broken lines were constructed by using eq 6 with appropriate parameters computed from equations of the continuous lines at 280° and 320° C. (See also table 6.) The continuous lines are drawn through experimental points.

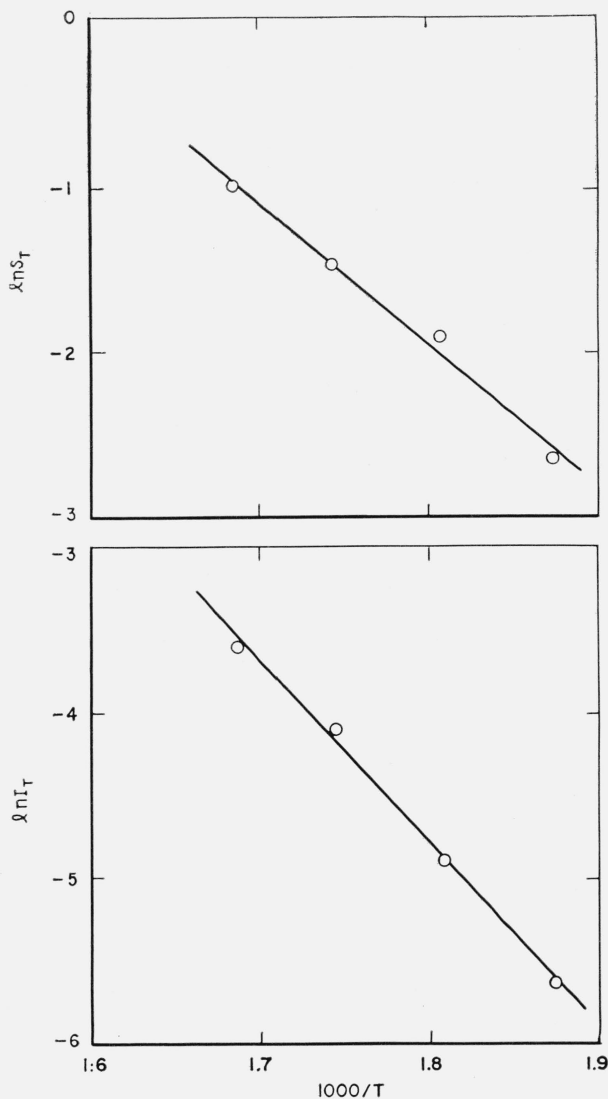


FIGURE 6. Logarithms of the slopes and intercepts, respectively, of the lines in figure 1 for char 1 (a coconut-shell charcoal) expressed as a function of the reciprocal absolute temperatures.

TABLE 7. Calculated values for the parameters of the relationship (eq 6), which expresses the rate constant as a function of oxygen concentration and temperature

	$E_1$	$E_2$	$A$	$B$
Char 1 (coconut-shell charcoal).....	cal 21,800	cal 16,900	1/hr $2.93 \times 10^6$	1/hr $6.09 \times 10^5$
Char 2 (new bone char)...	7,000	23,500	$4.10 \times 10^1$	$1.25 \times 10^9$
Char 35 (service bone char).....	16,200	43,200	$3.45 \times 10^4$	$1.09 \times 10^{15}$
Char 3 (service bone char).....	19,700	34,800	$1.16 \times 10^8$	$1.63 \times 10^{13}$
Char 27 (spent bone char).....	23,300	19,200	$5.37 \times 10^7$	$1.70 \times 10^7$

considering the change in the ratio of  $\text{CO}_2$  to  $\text{CO}$  with time of contact of the gases with the sample. The catalytic oxidation is not concerned with the consumption of carbon from the solid state; hence, the variation in the  $\text{CO}_2$  to  $\text{CO}$  ratio can not be expected to have any effect upon  $k$ . This point was also brought out earlier in the paper. The catalytic reaction may thus be eliminated in connection with the initial steps involved in the combustion process.

Of the many mechanisms that have been proposed in the past for the low temperature combustion of carbon, only a few are consistent with the experimental findings of this paper. Equation 6 contains two terms, both of which increase exponentially with the reciprocal of the absolute temperature; but only one depends upon oxygen concentration. This requires that two processes must be taking place independently. Furthermore, some, if not all, of the primary product must be  $\text{CO}$ , since  $\text{CO}$  is one of the products. A recent article by Strickland-Constable [25] reviewed the various mechanisms that have been proposed for the combustion of carbon at temperatures above and below  $1,000^\circ \text{C}$ . One mechanism contained in that paper applicable in the range of  $400^\circ \text{C}$  could easily be expanded to fit the experimental findings of this present investigation. It states: "Since the (surface oxygen) complex appears to be neither an intermediate product, nor reversibly adsorbed product, a remaining possibility is to consider it to be a by-product of the main reaction, which is only formed at certain favourable points on the surface. When once formed, the complex remains on the surface as a relatively stable body that is decomposed to the product only on raising the temperature." Insofar as the rest of the surface is concerned, the reaction could be first order with respect to oxygen. The decomposition of the stable complex need not be caused solely by raising the temperature. It could depend upon the acquisition of sufficient energy to decompose it at the reaction temperature and, hence, could very well be independent of oxygen concentration.

Another possibility is that the entire surface is covered with a single type of complex. This could then decompose to products in two ways, both taking place simultaneously. In the first way, the decomposition would be spontaneous depending upon the absorption of sufficient energy to decompose the complex at the reaction temperature



and thus be independent of the oxygen concentration. In the second way, the complex would combine with additional oxygen before decomposing to products such that this step would be proportional to the oxygen concentration.

A third possibility is that two distinct surface complexes are formed independently of one another. In the one case, the rate of decomposition of the complex (assumed to be much slower than its rate of formation) would be rate determining and, thus, be independent of oxygen concentration. In the other case, the rate of formation of the complex would be the slower and, hence, could very likely be proportional to oxygen concentration.

In any of the above processes the total reaction rate would, of necessity, be given by the sum of the two individual steps and lead to an expression of the form of eq 6. Whether one, if any, of these mechanisms is to be preferred depends upon additional experimental work beyond the scope of this paper. The existence of one, or more than one, species of complex taking part in the combustion process is a problem that might be answered from X-Ray diffraction measurements.

Surface-area studies may not be expected to throw any light on the extent of complex covering the surface. On the other hand, heats of adsorption of nitrogen for surfaces covered with complex as compared with surfaces partially denuded of complex might afford a means of estimating the extent of complex coverage.

A positive intercept on the  $k$  axis has been treated as though a finite initial reaction rate existed as the oxygen concentration approached zero. This may or may not be so. If, as shown in figures 1 through 5, the extrapolation below the lowest measured value of 0.02 is valid, it would imply the prior presence of chemisorbed oxygen. On the other hand, if the linear relationship breaks sharply as zero oxygen concentration is approached such that the reaction rate also goes to zero, this would imply an initial induction period. Such an initial process could be interpreted as the rapid formation of a chemisorbed oxygen layer. Further experimental work at very low oxygen concentration is required under conditions where the amount of chemisorbed oxygen were known and could be altered deliberately.

A possible reaction that has not been considered elsewhere in this paper is the reduction of carbon

by  $\text{CO}_2$  and its converse, the autooxidation of  $\text{CO}$ . At  $360^\circ\text{C}$  the equilibrium constant for the  $\text{CO}_2$  reduction of graphitic carbon is of the order of magnitude of  $10^{-6}$  [24]. No similar figure is available for the carbonaceous residues such as exist in carbon adsorbents. One may assume that it is about the same magnitude, since no measurable loss of carbon in bone char by reaction with pure  $\text{CO}_2$  was observed in independent experiments until temperatures in excess of around  $600^\circ\text{C}$  were used. The converse reaction would cause the formation of carbon brought about by the simultaneous oxidation and reduction of  $\text{CO}$ . No evidence exists as to whether this reaction takes place to any measurable degree under the conditions of this investigation. This point could be established, however, by treating carbon adsorbents with  $\text{CO}$  and testing for the presence of  $\text{CO}_2$  in the products. Radioactive tracer technique might also be employed to advantage in determining whether carbon is deposited.

## VII. Summary

1. A study was made of the rate of combustion with respect to carbon of carbon adsorbents below  $400^\circ\text{C}$  as a function of oxygen concentration and temperature.
2. Experimental results confirm the beliefs of earlier investigators that some of the carbon monoxide formed is oxidized catalytically to carbon dioxide as a secondary process. The extent of this secondary conversion is inversely proportional to the velocity of flow, other factors remaining constant.
3. The initial combustion rate at constant temperature depended linearly upon oxygen concentration.
4. The temperature dependence of initial combustion rate at constant oxygen concentration was expressed as the sum of two Arrhenius-type terms.
5. By combining the influence of oxygen concentration with that of temperature, a single relationship was obtained in terms of the initial reaction rate.
6. Activation energies (or free energies) of the Arrhenius-type terms were evaluated for the combustion of each of the five carbon adsorbents investigated.
7. Possible reaction mechanisms consistent with the experimental results were postulated.

## VIII. References

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