

THE CARBON-OXYGEN REACTION AT HIGH TEMPERATURES AND HIGH GAS FLOW RATES**

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This work was undertaken in order to expand available information on the carbon-oxygen reaction to high temperature-high gas velocity conditions.

The rate of petroleum-coke carbon combustion was found to increase proportionally with the square root of the gas injection velocity at carbon surface temperatures of 1500 and 2000°K. It was shown that the rate of petroleum-coke carbon consumption was directly proportional to the oxygen concentration from 37 to 100%, at all temperatures studied. The apparent activation energy for the combustion of petroleum-coke carbon decreased from 5.3 to 2.3 kcal./mole as the gas injection velocity increased from 5000 to 60,000 feet per minute. Nitrogen, helium, carbon dioxide and carbon monoxide were found to act merely as diluents during combustion, water vapour decreased the product CO/CO₂ ratio, and chlorine was found strongly to retard the combustion reaction.

These results primarily indicate the importance of using a high gas-injection velocity if rapid combustion rates of carbon are desired.

I. Description of the apparatus and character of the reaction

Introduction

Modern combustion and gasification processes frequently operate in the range of 1600° and higher where little or no data are available regarding either the mechanism or kinetics of the carbon-oxygen reaction. With a view to securing information primarily in the high-temperature range, the present investigation was initiated using an adaptation of the high-velocity technique employed by Grodzovskii & Chukhanov.¹ This high-velocity technique has been employed in an attempt to remove as much as possible the effects of diffusional films and interfering secondary reactions on the kinetics of the over-all carbon-oxygen reaction. This was deemed desirable so that information on the effect of the true chemical reactivity of different carbons on their combustion rates with oxygen at high temperatures could be studied.

Apparatus and procedure

In essence the method of attack, as shown in Fig. 1, consisted of impinging a jet of reactant gas at the centre and perpendicularly to the end of a carbon rod. The rapid flow of the gas stream past the surface served to sweep the primary reaction products away from the surface before significant secondary reaction had a chance to occur. The carbon rod was fed into the reaction chamber as fast as it was consumed so that the reacting surface was at the same location at all times.

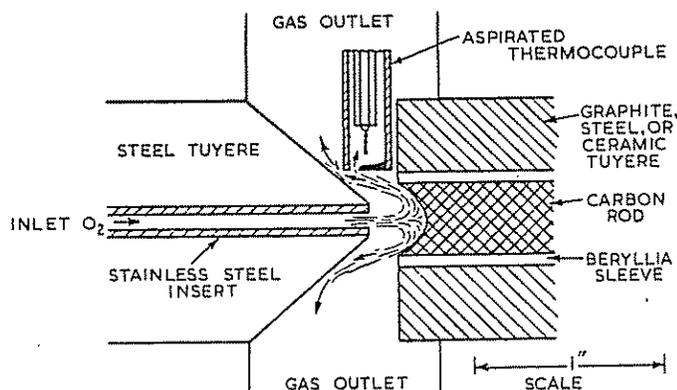


Fig. 1. Diagram showing position of tuyeres and carbon, observed lines of gas flow during run

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Reactor

The furnace was a steel cylinder 6 in. long by 6 in. in diameter. A $1\frac{1}{4}$ -in. diameter hole along the central axis of the cylinder admitted the fuel and blow tuyeres, which were mounted coaxially and faced each other. A $\frac{5}{8}$ -in. hole, drilled horizontally and perpendicularly to the tuyeres, provided two portholes—one through which the operator could watch the progress of the reaction and the other through which a photocell could be focused on the reacting carbon face and thereby control its rate of advance during combustion. A $\frac{5}{8}$ -in. diameter ignition port drilled at approximately 45° to the axis of the tuyeres, enabled the lowering of another carbon rod into the apparatus. This carbon, along with the test carbon, formed the elements of an electric arc used to raise the temperature of the test carbon prior to ignition.

Tuyeres

Steel and graphite fuel tuyeres, having an inner sleeve lining of mullite, were used in comparatively low-temperature experiments, and a $\frac{1}{16}$ -in. thick pure beryllia sleeve was used in high-temperature work. Tests showed that changing the materials comprising the tuyeres or the liners did not effect the product gas compositions under the reaction conditions imposed. In order to exert some measure of control over the reaction temperature, a water-cooled stainless steel tuyere and an electrically heated, all-ceramic tuyere, were also used.

Both stainless steel and water-cooled gas injection tuyeres were used. These tuyeres had stainless steel inserts which fit snugly into their gas exit end. These inserts had internal diameters ranging from 0.028 to 0.144 in. and served as an effective means of varying the size of the impinging gas jet.

Treatment and measurement of injected gases

Fig. 2 presents a flow diagram of the apparatus. Oxygen and small amounts of other gases were mixed in a common main before entering the combustion furnace. Spot chemical analyses indicated that mixtures of constant composition could be maintained in this way. When gaseous mixtures from the two meters were used, however, samples were always taken, and chemical analysis was relied upon as the ultimate standard. For some experiments where preheating of the injected gases was used, the gases were passed through a Fisher gas-fired superheater before entering the blow tuyeres.

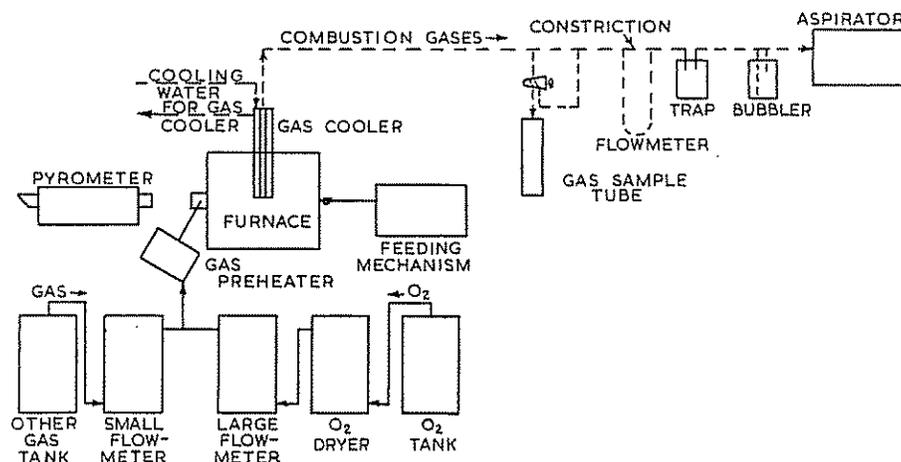


FIG. 2. Flow diagram of apparatus

Sampling and analysis of gaseous products

Samples of the product gases were aspirated through a gas cooler, shown in Fig. 1, placed as close to the reacting surface as possible without disturbing the flow of gas to the carbon

surface and the surface temperature. The gas cooler was packed with stainless steel helices to increase the amount of cooling surface and to facilitate mixing of the gases before the sample was taken. After the gases were aspirated through the cooler, they were passed through a tube where a fraction was continuously drawn off into a gas-sampling bottle and stored over a brine solution composed of 20% Na₂SO₄ and 5–10% H₂SO₄. The gases were analysed in a conventional gas-analysis apparatus.

Apparatus for ignition of carbon rods

An insulating ceramic sleeve and igniter carbon were lowered into the ignition port, and an arc between the igniter carbon and the test carbon drawn. Several minutes after the arc had been struck, the oxygen was turned on and the reaction proceeded under its own heat. The following sequence of events then took place: the arc was turned off, the igniter carbon and ceramic sleeve were withdrawn, the ignition port was closed, and the blow tuyere was slid in and secured in place. A test was then ready to be started.

Temperature measurements

A Pyro optical pyrometer was mounted outside the window of the injection tuyere and within 14 in. of the carbon face to record reaction temperature. The temperature of the steel reaction furnace was followed with a chromel–alumel thermocouple imbedded in a well in the steel block and connected to a Bristol recorder. The temperature of the injected gases was measured by placing a thermocouple, insulated from contact with the furnace, in the position of the carbon face and then flowing the gas upon it at the various rates of flow. The temperature of the product gases was measured by lowering an aspirated thermocouple as close as possible to the reaction pocket in the carbon rod.

Carbons

Five types of rod carbons, $\frac{3}{8}$ -in. and $\frac{1}{2}$ -in. in diameter, were used in the investigation.*

1. *Petroleum-coke-base carbons.*—These rods were made by extruding a mixture of 75% petroleum-coke flour (70% through 200 mesh) and 25% coal-tar pitch. The gas-baked carbon resulted from baking the extruded rods at a temperature of approximately 1000° for several weeks.

2. *Anthracite-base carbons.*—These rods were produced in essentially the same manner as the petroleum-coke-based rods. The original coal used for these rods was a medium-volatile anthracite, selected especially for its low ash content.

3. *Lampblack-base carbons.*—Because of the difficulty of obtaining a good bond between the lampblack and coal-tar pitch, the lampblack and coal-tar pitch were mixed, extruded and baked again. In this way, the amount of binder used was as high as 40%.

4. *Graphitized carbons.*—Graphitized carbons from lamp black and anthracite were examined in the work. These rods were produced by graphitizing the carbons at approximately 2500° for about 12 hours.

Chemical analyses of the test carbons.—The chemical analyses are shown in Table I. It cannot be readily explained why the volatile matter content of the graphitized anthracite is higher than that of the anthracite-base carbon. A repeat analysis on separately prepared samples also resulted in a higher volatile matter content for the graphitized anthracite.

Table I
Chemical analyses of carbon rods

	Carbons			Graphitized carbons	
	Petroleum-coke	Lamp-black	Anthracite	Lamp-black	Anthracite
Loss at 105°, %	0.1	0.1	0.1	0.1	0.1
Volatile matter, %	0.7	0.4	0.2	0.4	0.5
Ash, %	0.9	0.3	4.6	0.1	0.3
Sulphur, %	0.9	0.4	0.7	0.0	0.3
Carbon, %	97.3	98.7	94.3	99.4	98.7
Hydrogen, %	0.1	0.1	0.1	0.0	0.1

*Supplied through the courtesy of H. W. Abbott, Speer Carbon Company.

Crystallinity of test carbons.—X-ray diffraction patterns of the carbons were taken to determine their relative degrees of crystallinity. The samples were prepared by placing 0.150 g. of — 325-mesh material on a glass slide and dispersing the carbon with a mixture of 20% collodion in amyl acetate so that the sample covered an area of about 1 sq. in. A 90° (2θ) Norelco spectrometer was used for the work. The height of the (002) diffraction peak of the carbons was measured and the data presented in Table II. The relative crystallinity was arbitrarily based on a value of 100 for the graphitized lampblack carbon, which gave the highest peak.

Table II
Relative crystallinity of carbon rods

Type of carbon	Height of peak	Relative crystallinity
Graphitized lampblack-base	6.2	100
Graphitized anthracite-base	3.7	61
Lampblack-base	1.5	24
Petroleum-coke-base	2.2	36
Anthracite-base	0.3	4.8

Spectrographic analyses of the test carbons.—The spectrographic analyses were performed by the National Spectrographic Laboratories, Inc., Cleveland, Ohio. Table III presents the results which are indicative of the approximate impurity levels between the samples.

Table III
Spectrographic analyses of carbon rods

Type of Carbon	Carbons			Graphitized carbons	
	Petroleum-coke	Lamp-black	Anthracite	Lamp-black	Anthracite
Vanadium	0.00x	0.000x	0.000x	Absent	0.00x
Aluminium	0.00x	0.00x	0.0x	0.000x	0.000x
Titanium	0.000x	0.000x	0.00x	Absent	0.00x
Boron	0.00x	0.0x	0.00x	0.000x	0.0x
Tin	0.00x	0.000x	0.00x	Absent	Absent
Calcium	0.0x	0.00x	0.000x	0.00x	0.0x
Nickel	0.00x	0.000x	0.000x	0.000x	0.000x
Copper	0.00x	0.00x	0.00x	0.000x	0.000x
Iron	0.0x	0.0x	0.0x	0.000x	0.00x
Lead	0.00x	0.000x	0.0x-0.0x	0.000x	0.000x
Magnesium	0.0x-0.0x	0.0x	0.0x-0.0x	0.000x	0.000x
Manganese	0.000x	0.000x	0.00x	0.000x	0.000x
Silicon	0.0x	0.0x	0.0x	0.000x	0.00x
Sodium	0.0x	0.0x	0.0x	0.000x	0.000x

Results

Factors affecting shape of reacting surface

The reaction on the carbon surface quickly stopped when the oxygen blast was turned off. Thus, it was possible to preserve the surface for measurement and close examination. Preliminary experiments indicated that above a certain minimum flow velocity, the shape and depth of the crater hollowed out of a reacting carbon end remained constant for a particular diameter of carbon rod and blow tuyere used, being independent of carbon-face temperature, inlet-gas composition and inlet gas velocity. For example, when blasting a $\frac{3}{8}$ -in. diameter petroleum coke rod with the jet from a 0.091-in. diameter tuyere, this 'minimum' flow velocity was 10,000 feet per min. From 10,000 to 60,000 feet per minute (the maximum possible flow rate obtainable), the shape of the carbon end remained the same. Below 10,000 feet per minute, the crater began to deepen, exposing more carbon surface for reaction. The 'minimum' flow velocity at which the depth of the crater became constant increased with decreasing diameter of tuyere. The depth of the crater in the carbon face, formed at 'minimum' flow velocity, was also found to increase with decreasing diameter of blow tuyere.

Repeated experiments showed that the surface of the reacted carbon assumed an equilibrium shape and size at some interval after the reaction was started. Furthermore, under identical operating conditions this surface could be readily duplicated between runs. For the 0.091-in.

diameter tuyere (used exclusively in the subsequent papers) the equilibrium surface was assumed within the first 1/4-in. length of rod reacted. It should be emphasized that in the experiments to be reported later all measurements were made and gas samples taken only after it was certain that the equilibrium surface had been established.

Calculation of external carbon surface areas

In order to obtain the shape of the reacted end of the rods, they were cut in half longitudinally and the outline of the rod's diameter and the reaction cavity transferred by means of carbon paper to a piece of thin tracing paper. The tracing paper was then placed in a photographic enlarger and projected on to a sheet of graph paper with an enlargement of 7.9 times.

In Fig. 3 are plotted the dimensions of the cavities produced in a 3/8-in. diameter petroleum coke rod by the 0.091-in. blow tuyere at different times until an equilibrium surface was reached. Equations of the straight lines are of the form, $y = ax^{0.50}$, characteristic of a parabolic shape for

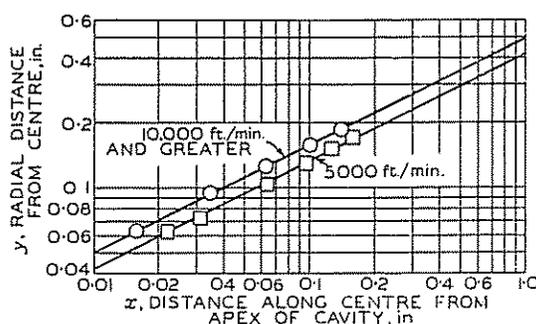


Fig. 3. Actual dimensions of centre section of surface produced by 0.091 in. blow tuyere on 3/8-in. diameter petroleum-coke carbon rods

the crater. For the 10,000 feet per minute or higher flow rate, the equation is $y = 0.50 x^{0.50}$. This expression can then be substituted into the equation for the generation of a surface of revolution

$$S = 2\pi \int_0^x y \left[\left(\frac{dy}{dx} \right)^2 + 1 \right] \cdot dx \dots \dots \dots (1)$$

and using as limits $x = 0$ and $x = 0.141$ inch, the equilibrium carbon surface area is found to be 1.03 sq. cm. (It should be emphasized here that doubtless the equilibrium carbon surface contains some micro-surface roughness which has been ignored in this calculation but the surface calculated for the macro-shape of the reacting surface is thought to be proportional to the true reacting surface area). A similar procedure has been carried out for all carbons investigated and the data for equilibrium crater depth, surface area and volume developed by flow

Table IV

Dimensions for the equilibrium shapes of carbons produced by combustion at flow velocities greater than 10,000 ft. per min.

Type of carbon	Crater depth, cm	Surface area, sq. cm.	Volume, c.c.
Petroleum coke	0.358	1.03	0.129
Lampblack	0.300	0.93	0.104
Anthracite	0.221	0.80	0.085
Graphitized lampblack	0.358	1.03	0.129
Graphitized anthracite	0.358	1.03	0.129
Petroleum coke at 5,000 ft. per min.	0.475	1.16	0.159

velocities of 10,000 feet per minute and higher, with the 0.091-inch diameter tuyere, are given in Table IV. Similar data for the surface generated by the 5000-ft. per minute velocity on

petroleum coke is included for purposes of comparison. The crater volumes have been calculated by substituting the parabolic equations for crater shape of each carbon in the equation for a volume of revolution

$$V = \pi \int_0^x y^2 dx \dots\dots\dots (2)$$

It is seen from Fig. 3 that the depth of the crater developed in petroleum coke at 5000 ft. per min. is deeper than that for higher flow rates. A calculation of the Reynolds number for 5000 ft. per min. velocity of flow through the 0.091-inch diameter tuyere gives a value of 4000, which is in the transition range between streamline and turbulent flow. Velocities through this tuyere of 10,000 feet per minute and greater give Reynolds numbers well in the turbulent region. Therefore, it is seen that the depth and shape of the crater are dependent upon the nature of flow emerging from the tuyere.

Pressure distribution on reacting carbon surface

The impact pressure on the carbon surface was measured in the following way. After the equilibrium surface had been generated, a 1/8-in. diameter hole was bored along the central, longitudinal axis of the carbon rod. This part of the hole in the end of the rod opposite the reaction face was enlarged just to allow an 3/8-in. diameter steel tube to be snugly fitted into the hole. One end was connected to a manometer. The carbon rod was then inserted into the furnace in its normal position, oxygen turned on and the impact pressure measured for various flow rates. The same procedure was repeated for other positions toward the outside periphery of the rod.

A diagram showing the location of the holes drilled in a 1/2-in. petroleum-coke carbon rod and the pressures obtained with the 0.091-in. tuyere is shown in Fig. 4. The outside pressure taps were filled with cement around a small rod placed in the opening so that the diameter of the hole would be 1/8-in. and its opening would be perpendicular to the carbon face. In the absence of more definite knowledge concerning the oxygen concentration along the carbon surface, the impingement pressure at the vertex has been taken as a relative measure of the number of impacts per unit surface per unit time over the entire surface for the various rates of flow.

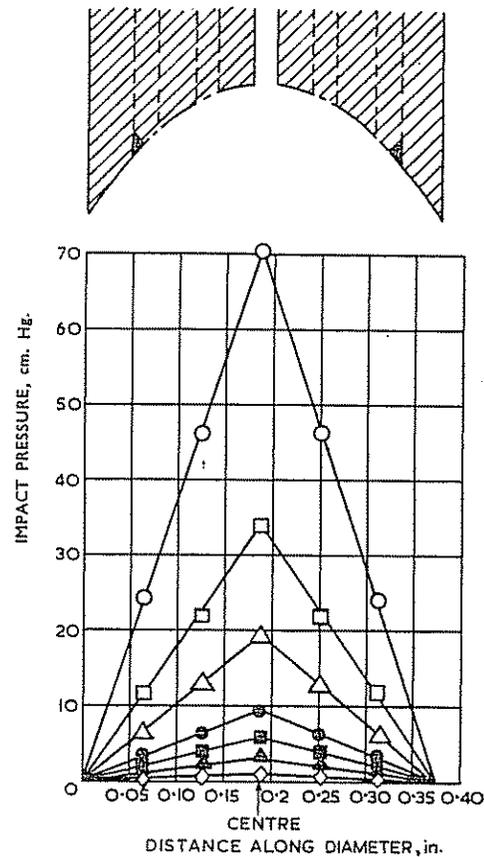


FIG. 4. Pressure distribution on carbon surface for 0.091-in. inlet tuyere on 1/2-in. petroleum-coke rod

- Gas inlet velocities
- 60,000 ft./min.
 - 40,000 ft./min.
 - △ 30,000 ft./min.
 - 20,000 ft./min.
 - 15,000 ft./min.
 - ▲ 10,000 ft./min.
 - ◇ 5000 ft./min.

Contact time

The contact time, or average time of residence of the injected oxygen in the reaction zone, was taken as the time required to renew the volume composing the crater in the reaction end of the carbon rods. This time was obtained by dividing the calculated volume of the crater by the volume of gas injected per unit time. The temperature of the gases coming from the reaction

pocket, measured as shown in Fig. 1, varied from 300 to 500°, depending on the velocity of gas flow, oxygen concentration and type of carbon. Since, at best, the temperature of the gases in the crater could only be measured roughly, the volume of the injected gas was calculated at conditions of 400° and the average pressure in the crater. Table V presents the variation in contact time with inlet velocity for the $\frac{3}{8}$ -in. diameter petroleum-coke carbon and the 0.091-in. tuyere, using the previously discussed data on the shape of the crater to determine crater volumes. The contact times for other carbons are of the same order of magnitude.

Table V

Variation of contact time with injection velocity for $\frac{3}{8}$ in. petroleum-coke carbon rods

Injection velocity, ft./min. at 24° and 1 atm.	Contact time, min., $\times 10^{-3}$
5000	10.8
10,000	4.40
15,000	3.00
20,000	2.29
30,000	1.63
40,000	1.33
60,000	1.07

Effect of tuyere size on the CO/CO₂ ratio in the product gas

Table VI presents data on the effect of injection tuyere size on the CO/CO₂ ratio obtained in the product gas and the extent to which reaction may occur, for both the $\frac{3}{8}$ and $\frac{1}{2}$ -in. diameter petroleum-coke carbons. The percentage conversion of oxygen increases with decreasing diameter of blow tuyere, but higher injection velocities must be employed to keep secondary reactions at a minimum when using the smaller tuyeres. The percentage oxygen conversion for the 0.091-in. tuyere and $\frac{3}{8}$ -in. rod was nearly the same as the conversion for the 0.118-in. tuyere and $\frac{1}{2}$ -in. rod for the same injection velocity. The ratio of carbon to tuyere diameter is nearly equal for these two combinations, being 4.12 and 4.24, respectively. Furthermore, for each ratio of carbon diameter to injection tuyere size, the oxygen conversion was a function of the velocity only, remaining essentially constant for oxygen concentrations from 36 to 100% and over the temperature range 1500–2300°K.

For the later experiments reported, $\frac{3}{8}$ -in. diameter rods and the 0.091-in. injection tuyere have been used in order to limit the number of variables studied.

Table VI

Effect of injection tuyere size and injection velocity on the CO/CO₂ ratio and extent of reaction for $\frac{3}{8}$ -in. and $\frac{1}{2}$ -in. diameter petroleum-coke carbon rods

Tuyere diameter, in.	Injection velocity at 24° and 1 atm., ft./min.	Carbon surface temp., °K	CO/CO ₂ ratio	Oxygen conversion %
		$\frac{3}{8}$ -in. diameter rods		
0.047	67,700	1970	1.53	26.7
0.047	68,000	2005	1.6	26.6
0.0625	13,000	1930	0.022	46.2
0.0625	22,000	2065	0.035	35.2
0.0625	42,000	2138	1.25	22.6
0.0625	58,000	2210	5.9	12.0
0.091	10,000	2035	2.96	14.1
0.091	20,000	2080	3.5	9.4
0.091	30,000	2175	5.9	7.5
0.091	60,000	2300	11.0	5.5
0.118	20,000	1710	0.69	6.0
0.118	20,000	1875	0.91	6.2
0.118	35,000	2195	6.8	3.4
		$\frac{1}{2}$ -in. diameter rods		
0.118	10,000	2035	1.74	15.3
0.118	20,000	2100	3.6	9.5
0.118	30,000	2170	4.9	7.3

II Kinetics of the reaction between 1500 and 2300°K

Introduction

Heterogeneous reaction rates involving a porous solid and a gas may be controlled by one or more of three major steps:

(1) Mass transport of reacting gas and product or products across a relatively stagnant gas film between the exterior surface of the solid and the main gas stream.

(2) Mass transport of the reacting gas from the exterior surface to an active site beneath the surface and mass transport of the products in the opposite direction.

(3) Adsorption of reactant, chemical reaction between reactant and active site, and desorption of product.

In essence, if the resistances of steps (1) and (2) are low in comparison with that of step (3), the concentration of reacting gas both at the exterior and interior surface of the solid is equal to the concentration in the main gas stream. Since the chemical reactivity of the solid, step (3), usually increases with temperature more rapidly than steps (1) and (2), temperatures are reached, first, where the resistance of step (2) becomes significant and then step (1) also becomes significant. The resistance of step (2), at a given temperature, is primarily determined by the size and degree of inter-connection of the pores within the solid and cannot be significantly altered in a given carbon, the result being that the percentage of the reaction occurring close to the exterior surface of the solid increases markedly with increasing reaction rate. The resistance to step (1) can be easily decreased by increasing the gas flow rate past the exterior surface of the solid, which in turn decreases the film thickness. This results not only in a faster rate of mass transport through the film but also in a higher concentration of reactant at the surface by decreasing secondary reactions in the film.

In the case of the strongly exothermic carbon-oxygen reaction, surface temperatures are easily reached where the rate of combustion is controlled by steps (1) and (2). The majority of the work in the past²⁻⁶ on the carbon-oxygen reaction has been devoted to investigating the change in the reaction rate as the gas flow rate was increased, while still being considerably in the range where the rate was controlled by steps (1) and (2). The partial control of the reaction by step (2), as discussed previously, means that the reaction occurs almost entirely on the outer surface of the carbon, thereby utilizing only a small fraction of the carbon for reaction. This in turn results in a reaction rate which is only a small fraction of what it would be if the entire surface of the carbon, exterior and interior, were exposed to the reactant at unit concentration. In other high-temperature investigations, as in this, it should be pointed out that step (2) is always the controlling resistance, in the above sense; but future discussion regarding it, considering the problem at hand, is unnecessary.

Kuchta, Kant & Damon⁷ investigated the combustion rate of spectroscopic-grade electrode carbon in a high-velocity air stream. They have shown that reaction rates are essentially independent of oxygen preheat temperature between 900 and 1200° but vary with the 0.45 power of flow velocity over the range 1700 to 32,500 feet per minute. This they show is in agreement with theoretical calculations in which mass transport to the external carbon surface is assumed to be the rate-controlling factor. These authors also show that their experimental data agree in general with the Arrhenius-type equation, assuming chemical reactivity, step (3), to control, if an activation energy of 20 kcal. per mole and surface temperatures of the reacting carbon are used. The final conclusion is that under these conditions the reaction of carbon and oxygen lies in an intermediate region where both mass transport to the external surface and chemical reactivity are rate controlling factors.

With this in mind, the present investigation has been carried out at gas velocities up to 60,000 feet per minute to examine the effect of very high flow rates on the rate controlling mechanism. The experimental apparatus, procedure, and a description of reactants have been covered in Part I.

Results

Factors affecting CO/CO₂ ratio

As the injection velocity was increased, the temperature of the carbon face and the CO/CO₂ ratio increased. It was desirable to separate these variables in order to determine whether

velocity or temperature, or both, influenced this ratio. Two methods were utilized to vary the reaction temperature independently of the velocity: (1) A temperature range of 300 to 400° was obtained by employing a variety of fuel tuyeres, i.e., water-cooled, heated, etc.; (2) oxygen concentration was decreased by dilution with nitrogen. Fig. 5 shows that the CO/CO₂ ratio was independent of the oxygen concentration at a velocity of 20,000 feet per minute and was dependent on the temperature, the ratio increasing steadily as the temperature increased above 1800°K.

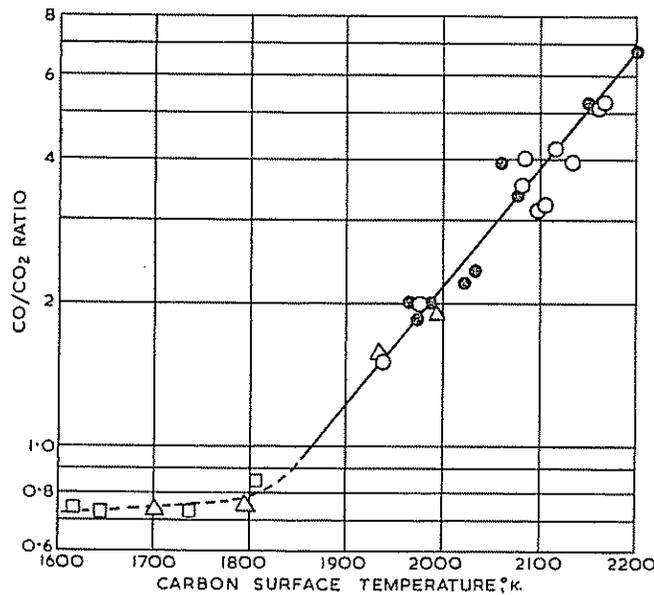


FIG. 5. Independence of CO/CO₂ ratio of the oxygen concentration for petroleum-coke carbon at 20,000 ft./min. inlet velocity

● 99.6% oxygen △ 52.0% oxygen
○ 69.0% oxygen □ 36.7% oxygen

Fig. 6 demonstrates that the CO/CO₂ ratio was essentially independent of injection velocity above 10,000 ft. per min., the points over the range of velocities from 10,000 to 60,000 ft. per min. falling essentially along the same curve. These data suggest that the velocity at which the reaction products were swept from the surface was sufficient, at 10,000 ft. per min. and greater, to prevent appreciable secondary reactions in the gas phase. This was not the case at 5000 ft. per min., as is seen in Fig. 6. Visual observation also showed that a definite change in reaction conditions occurred when the velocity was increased from 5000 to 10,000 ft. per min.; the flame observed (undoubtedly being the oxidation of carbon monoxide to carbon dioxide in the gas phase) at the lower velocity disappeared as the velocity was increased. At temperatures below 1800°K., only a small part of the carbon monoxide was consumed by secondary reactions even at 5000 ft. per min. velocity; but above 1800°K the rate of flame propagation exceeded this relatively low velocity of product removal and secondary combustion occurred to a large extent.

The effect of the type of carbon on the CO/CO₂ ratio

Fig. 7 presents data for the CO/CO₂ ratio versus temperature of the carbon surface for all five carbons investigated at a gas velocity of 20,000 ft. per min. This ratio is seen to be essentially the same for petroleum-coke, graphitized lampblack and graphitized anthracite. On the other hand, both the lampblack and anthracite-base carbons gave an appreciably higher CO/CO₂ ratio. Since the amount of gas-phase oxidation of carbon monoxide would be expected to be roughly the same at identical gas velocities and surface temperatures, the implication is that both carbon monoxide and carbon dioxide were primary products of the surface reaction.

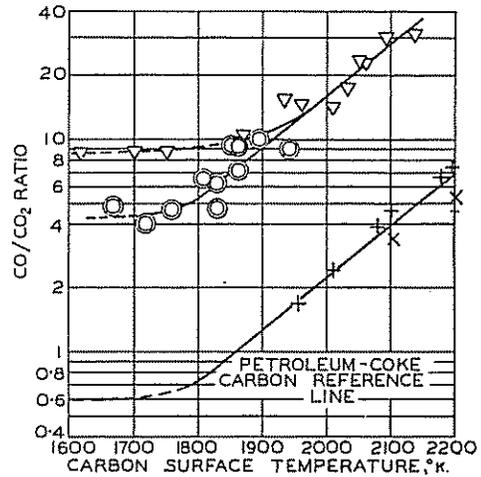
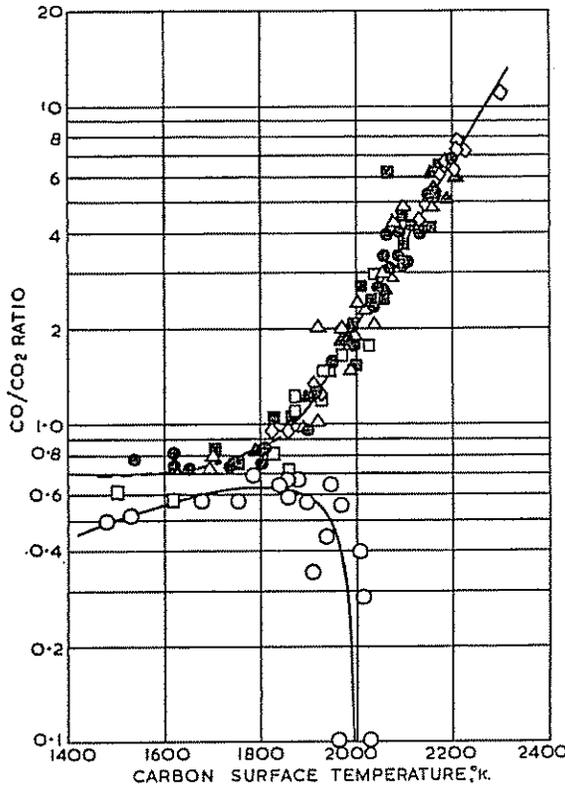


Fig. 7. Effect of different forms of carbon and the effect of change in the form of carbon (through graphitization) on CO/CO_2 ratio

- ▽ lampblack-base carbon
- anthracite-base carbon
- × graphitized lampblack
- + graphitized anthracite

Fig. 6(l). Effect of temperature on CO/CO_2 ratio and the independence of CO/CO_2 ratio of the inlet velocity of oxygen for petroleum-coke

- Inlet gas velocities
- 5,000 ft./min.
 - 10,000 ft./min.
 - △ 15,000 ft./min.
 - ⊙ 20,000 ft./min.
 - 30,000 ft./min.
 - ▲ 40,000 ft./min.
 - ◇ 60,000 ft./min.

There is, however, no apparent correlation between the CO/CO_2 ratio and the known properties of the carbons, such as, ash content, amount or type; hydrogen or sulphur content; relative crystallinity; and particle size of the starting carbon.

Effect of temperature and oxygen concentration on carbon consumption

The effect of temperature and inlet oxygen concentration, in oxygen-nitrogen mixtures, on consumption rate of petroleum-coke for an injection velocity of 20,000 ft. per min., is shown in Fig. 8. The carbon consumption is plotted in terms of g. of carbon consumed per min. per sq. cm. of the equilibrium carbon surface exposed to reaction per unit oxygen concentration. A temperature variation of roughly 300° was obtained for each gas composition by using either the water-cooled, plain or electrically heated fuel tuyere.

Using the data of Fig. 8, cross-plots are made of the carbon consumption *versus* the % oxygen in the injected gas stream at different constant temperatures, as shown in Fig. 9. The data indicate a linear increase in rate with increasing oxygen concentration. The 1900°k plot is within the range of experimental data presented in Fig. 8, while the 1600 and 2200°k plots are the result of extrapolations for the most part, but considering the steady trend exhibited in Fig. 8, these extrapolations appear reasonable.

Figs. 8 and 9 show that the carbon consumption rate is directly proportional to the oxygen concentration which would normally be expected, but has not been previously demonstrated for the particular temperature range or for oxygen concentrations from 37 to 100%. Parker & Hottel⁴ have shown this to hold for oxygen concentrations between 5 and 25% and for temperatures up to 1700°k. Gulbransen & Andrew⁸ report a first-order reaction between oxygen and spectroscopic graphite at pressures above 10 cm. Hg and at temperatures between 450 and 500°c. Meyer, working with a graphite filament in a high-velocity stream of oxygen at 5×10^{-2} mm. Hg pressure, found the reaction to be first-order at temperatures up to 1500°k.

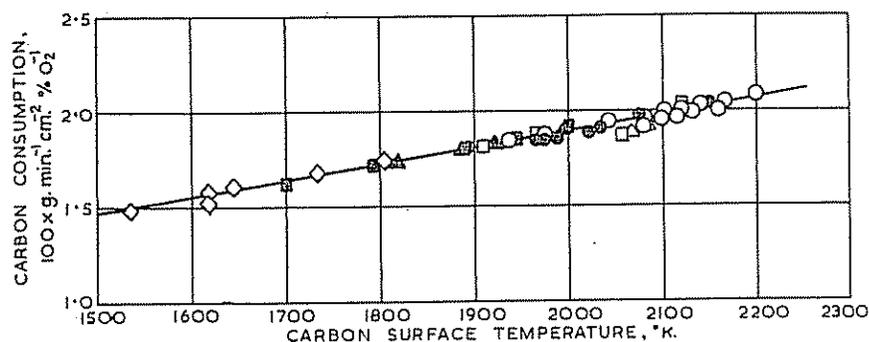


FIG. 8. Effect of temperature on petroleum-coke consumption at 20,000 ft./min. inlet velocity calculated to the bases of unit oxygen concentration

Oxygen concentration of blow

- | | |
|----------------|----------------|
| ○ 99.6% oxygen | ▲ 63.0% oxygen |
| △ 92.5% oxygen | ■ 52.0% oxygen |
| □ 84.0% oxygen | ◇ 36.7% oxygen |
| ● 69.0% oxygen | |

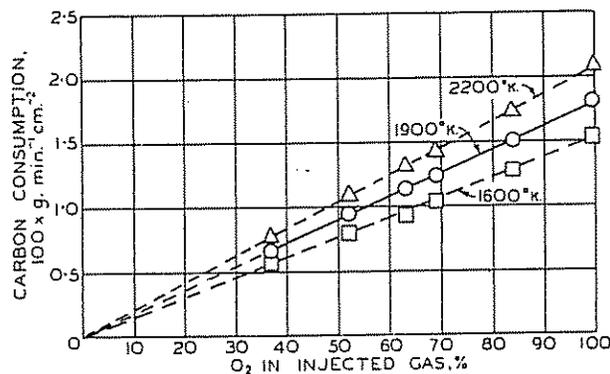


FIG. 9. Effect of oxygen concentration on the petroleum-coke consumption rate at constant temperature of carbon surface

The data from the other velocity experiments are treated in the same way and are presented in Fig. 10. These data are compared with those reported by Parker & Hottel,⁴ who reacted brush carbon with air of varying velocities. Their data are converted to unit oxygen concentration by dividing the carbon consumption rate by the fraction of oxygen concentration; and their air velocities at s.t.p. conditions, in terms of cm. per sec., are converted to ft. per min. These recalculated data are then plotted, along with the data in Fig. 10, in Fig. 11 for purposes of comparison. Since the lowest temperature in the experiments being reported was about 1500°K, the liberty of drawing in the dotted lines is taken based on the findings and indicated trends of Parker & Hottel.

Fig. 12 presents data for the rate of petroleum-coke consumption, in units of g. per min. per cm.² of surface per % oxygen, versus the ambient gas velocity at carbon temperatures of 1500° and 200°K. The ambient gas velocity is the actual efflux velocity from the tuyere nozzle, considering the increase in volume of the injected gas due to preheating by contact with the warm metal inlet tuyere. The rate of petroleum-coke consumption is found to increase proportionally with the square root of the velocity at both temperatures. The data of Parker & Hottel are also included for comparison. To a rough approximation, it was assumed that the air in their experiments had been preheated to 1200°K on passing through the apparatus, thus increasing the velocities four-fold over those reported at s.t.p. conditions. Although these increased velocities are used in Fig. 12, naturally the slope of this line is not changed, the rate varying with the 0.37 power of velocity. Mayers,³ using 40 by 60 mesh coke in 1-in. high beds, obtained a value of 0.5 for the exponent; Chukhanov & Karzhavina,¹⁰ in their high-velocity experiments using beds of particles 3 by 5.5 mm. in diameter found the reaction rate to increase linearly with

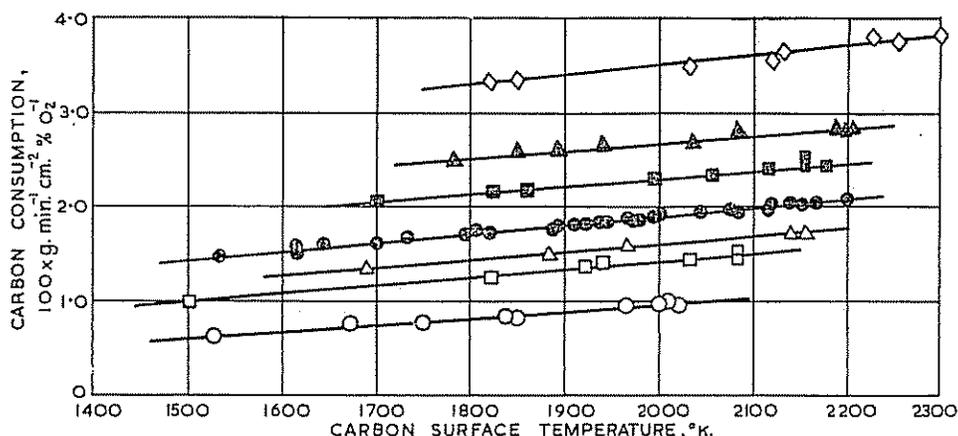


FIG. 10. Effect of temperature and linear inlet velocity, in ft./min. on petroleum-coke consumption

- ◇ 60,000 ft./min.
- ▲ 40,000 ft./min.
- 30,000 ft./min.
- 20,000 ft./min.
- △ 15,000 ft./min.
- 10,000 ft./min.
- 5000 ft./min.

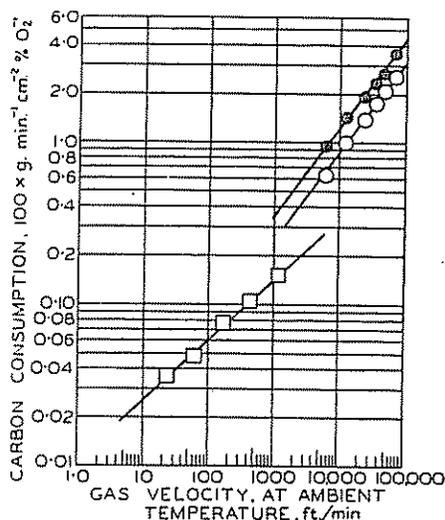
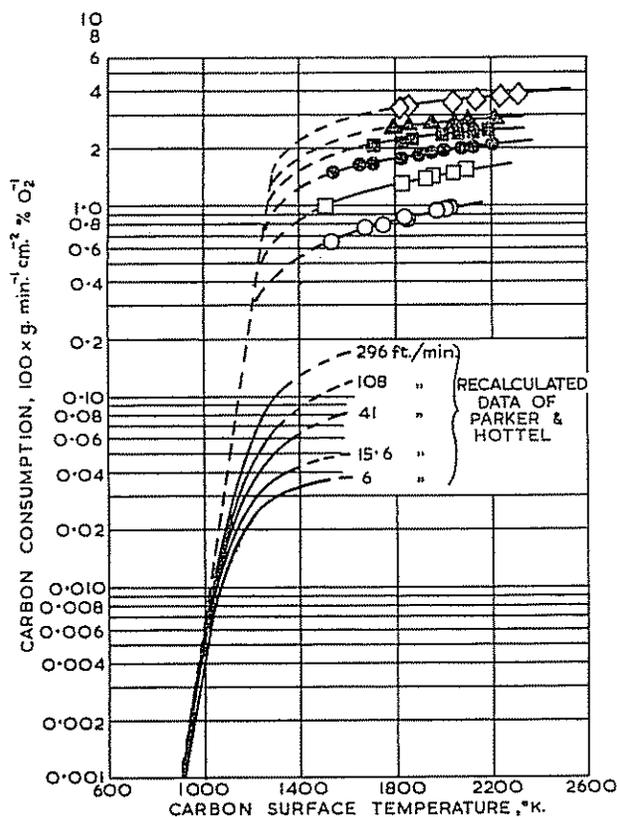


FIG. 12. Effect of gas velocity on the rate of carbon consumption

- petroleum-coke carbon at 2000°K
- petroleum-coke carbon at 1500°K
- data of Parker & Hottel, using brush carbon at 1500°K

FIG. 11. (l) Effect of temperature and inlet gas velocity on carbon consumption rate
All inlet velocities calculated at 24° and 1 atmosphere

- ◇ 60,000 ft./min.
- ▲ 40,000 ft./min.
- 30,000 ft./min.
- 20,000 ft./min.
- 10,000 ft./min.
- 5000 ft./min.

the 0.40 power of velocity ; and Kuchta *et al.*,⁷ using carbon rods, reported an exponent of 0.45. The agreement is fairly good considering the differences in the experimental techniques, extrapolations and different forms of carbons used.

The initial oxygen concentrations have been used for all calculations to date since they are the easiest and most reliable to obtain. If the oxygen concentration is taken as that found in the

product gas analysis, each curve in Fig. 10 is raised a proportional amount along the ordinate, the spacing between curves and the slopes being changed insignificantly.

In the absence of direct experimental data concerning the oxygen concentration at the carbon surface, the impingement pressure at the vertex of the carbon crater is taken as a relative measure of the number of impacts per unit surface area per unit time over the entire surface for the various rates of flow. These pressures in terms of atmospheres are divided into the corresponding petroleum-coke carbon consumption rates, shown in Fig. 10; and the results are plotted in Fig. 13. This shows that above 30,000 feet per min. injection velocity, no material increase in reaction rate, based on unit oxygen concentration and unit pressure, was realized.

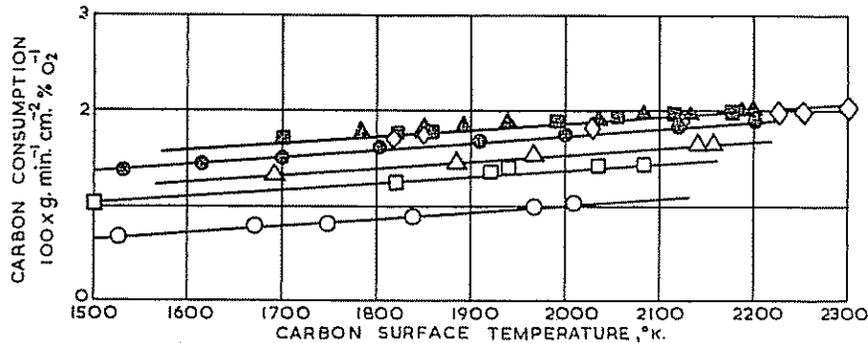


FIG. 13. Effect of temperature and injection velocity on petroleum-coke carbon consumption, based on unit oxygen concentration and unit pressure

Injection velocities calculated at 24° and 1 atmosphere

- 5000 ft./min.
- 10,000 ft./min.
- △ 15,000 ft./min.
- ⊙ 20,000 ft./min.
- ⊠ 30,000 ft./min.
- ▲ 40,000 ft./min.
- ◇ 60,000 ft./min.

Effect of preheating the injected gas

The effect of preheating the oxygen on the petroleum-coke carbon combustion rate is shown in Fig. 14. The injection velocity of 20,000 feet per min. was calculated as the volume of gas injected at 24° and 1 atmosphere. In preheating the gas, the volume and inlet velocity were increased accordingly, so that the actual efflux velocity of oxygen preheated to 300°, for example, would be 38,500 ft. per min. A reasonably close efflux velocity, 34,000 ft. per min. could also be obtained by passing 30,000 ft. per min. of oxygen at 24° and 1 atmosphere, but heated to 62°, the normal efflux temperature of the oxygen at this injection velocity. In turn, the carbon

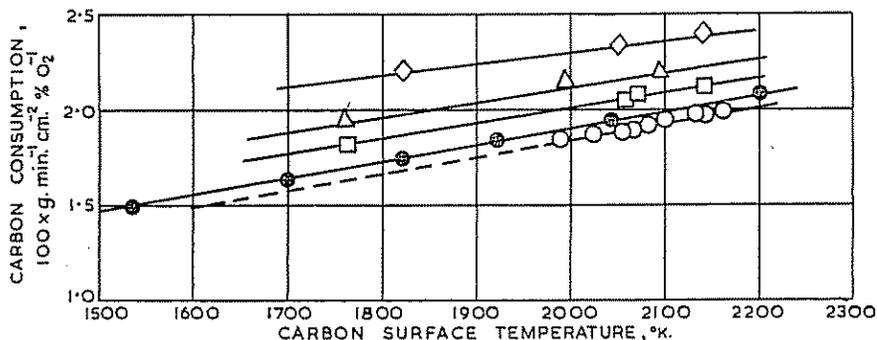


FIG. 14. Effect of preheating oxygen on the consumption of petroleum-coke carbon, at inlet velocity of 20,000 ft./min.

Velocities calculated at 24° and 1 atmosphere

Preheat temperatures

- 20°
- ⊙ 70°
- 150°
- △ 200°
- ◇ 300°

consumption rate for oxygen preheated to 300°, shown in Fig. 14, closely coincides with the 30,000 ft. per min. curve shown in Fig. 10. Therefore, preheating the oxygen appears only to increase the injection velocity and impinging pressure and have no direct effect on combustion rate. This agrees with the findings of Kuchta *et al.*,⁷ who found the rate independent of oxygen preheat temperature between 900 and 1200°.

Effect of gas injection velocity on activation energy

The rate equation for the carbon-oxygen reaction may be expressed as

$$-\frac{dC}{dt} = k C_c C_{O_2} \dots \dots \dots (3)$$

where *k* is the specific rate constant, *C_c* is the concentration of reacting carbon surface and *C_{O₂}* is the oxygen concentration at the surface. If the concentration of the reacting carbon surface is taken to be proportional to the equilibrium surface of the carbon crater and the oxygen concentration is taken as that of the inlet gas stream, the specific reaction rate constant can be expressed in units similar to the rate in Fig. 10. Then using the Arrhenius concept, *k*=*Ae^{-E/RT}*, these data are plotted in Fig. 15, resulting in a family of straight lines each representing a particular flow velocity. The slopes of the lines vary slightly, decreasing with increasing velocity as shown in Table VII.

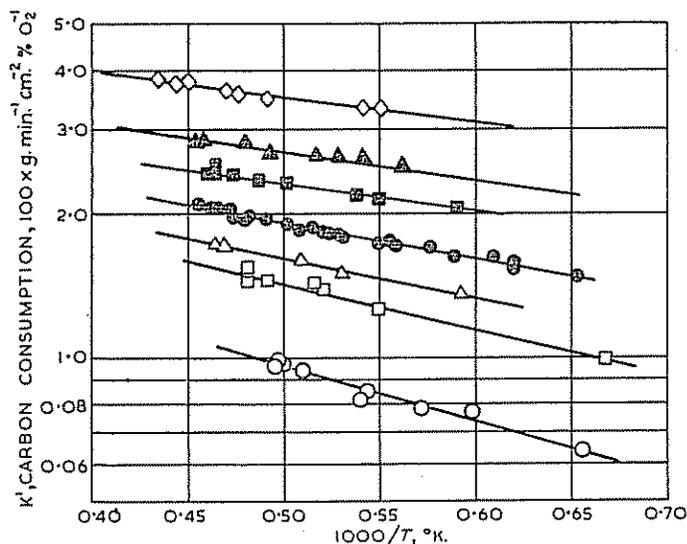


FIG. 15. Apparent Arrhenius relationship for petroleum-coke

Velocities calculated at 24° and 1 atmosphere
 ◇ 60,000 ft./min. △ 15,000 ft./min.
 ▲ 40,000 ft./min. □ 10,000 ft./min.
 ■ 30,000 ft./min. ○ 5,000 ft./min.
 ⊗ 20,000 ft./min.

Table VII

Variation of apparent activation energy with gas injection velocity for petroleum-coke combustion

Injection velocity, ft./min.	Apparent activation energy, cal./g.-mole (equation 3)	Activation energy, cal./g.-mole (equation 5)
5000	5300	8000
10,000	4300	5700
15,000	3750	4850
20,000	3350	4200
30,000	2860	3800
40,000	2550	3200
60,000	2300	2700

It was concluded from Figs. 8 and 9 that the reaction was first-order with respect to oxygen. Further proof of this is shown as follows :

$$\text{Let } -\frac{\Delta C_{O_2}}{\Delta t} = k (C_{O_2,av.})^n \dots\dots\dots (4)$$

be taken as an expression for the reaction rate, where ΔC_{O_2} is the difference between the injection oxygen concentration and the final oxygen concentration appearing in the product gas analysis, Δt is taken as the contact time, and $C_{O_2,av.}$, the average of the initial and final oxygen concentration. A plot of $\log \frac{\Delta C}{\Delta t}$ versus $\log C_{O_2,av.}$ is shown in Fig. 16 for petroleum-coke, with an injection velocity of 20,000 feet per minute, giving a slope of one, indicating the reaction to be first-order.

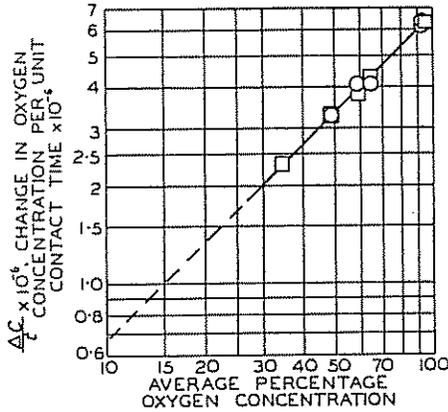


FIG. 16. Change in oxygen concentration per unit contact time for 20,000 ft./min. velocity at two temperatures

○ 2000°K □ 1900°K

The integrated form of the first-order equation

$$k = \frac{1}{t} \ln \left(\frac{C_{O_2,1}}{C_{O_2,2}} \right) \dots\dots\dots (5)$$

where $C_{O_2,1}$ and $C_{O_2,2}$ represent inlet and outlet oxygen concentrations, can then be used to calculate specific rate constants, which give equally as good Arrhenius plots as Fig. 15. Calculation of activation energies yields values of the same order of magnitude and shows the same trend as those previously calculated from the rate of carbon consumption, as seen in Table VII.

Reaction rates of different forms of carbon

The carbon consumption rates for lampblack- and anthracite-base carbons, at a velocity of 20,000 ft. per min., were calculated in the same manner as the petroleum-coke data and are plotted as a function of temperature as shown in Fig. 17. The reaction rate of the lampblack carbon is some 15% higher and of the anthracite carbon, 9% lower than that for the petroleum-coke.

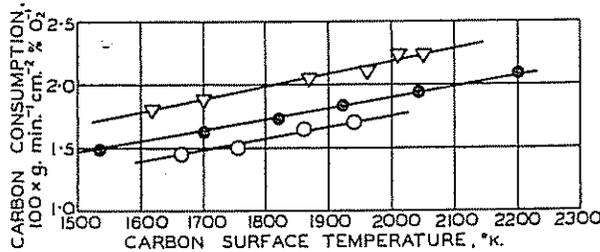


FIG. 17. Consumption of different forms of carbon at a constant inlet velocity of 20,000 ft./min.

▽ lampblack-base carbon
● petroleum-coke-base carbon
○ anthracite-base carbon

The greater heat conductivity of the graphitized rods rendered the experiments in which they were employed very difficult to control in the present apparatus. In order to prevent the reaction from being extinguished by the high heat losses, the electrically-heated fuel tuyere had to be used, along with preheating of the incoming oxygen. The ignition procedure used for the carbons could not be successfully employed for the graphites. Instead, a 1 to 1½-in. length of petroleum-coke rod was fastened to the end of the graphitized carbon rod by means of a tongue and groove cut into the ends of the rods, the petroleum-coke preceding the graphitized rod into the furnace. The petroleum-coke was easily ignited, reacted down and in turn ignited the graphitized rod. Once the graphitized rods were ignited the reaction proceeded smoothly provided the temperature of the apparatus and the injected oxygen was maintained high.

Only two experiments for each type of graphite were made under conditions such that a direct comparison with the behaviour of petroleum-coke could be made. Table VIII shows the data obtained from the graphitic carbons for oxygen preheated to 300° flowing at a velocity of 20,000 ft. per min. Points from previous figures, showing the behaviour of petroleum-coke at the corresponding temperature, are included for purposes of comparison. As can be seen, the agreement for the CO/CO₂ ratio is within experimental error and the differences in reaction rate are small.

Table VIII

Variation of carbon combustion rate and CO/CO₂ with type of carbon

Type of carbon	Temp. °K	CO/CO ₂ ratio	Carbon reacted, g. min. ⁻¹ cm. ⁻² %O ₂ ⁻¹
Graphitized lampblack	2080	3.6	2.17 × 10 ⁻²
Graphitized lampblack	2105	3.4	2.20
Graphitized anthracite	2100	4.6	2.09
Graphitized anthracite	2130	4.7	2.14
Petroleum-coke	2100	4.0	2.36

Discussion

The major results reported in this part of the paper are as follows:

- (1) The reaction rate was first-order with respect to the ambient oxygen.
- (2) The reaction rate increased directly with the 0.5 power of velocity of the impinging gas stream.
- (3) The reaction rate increased slightly with increase in temperature in the range 1500 to 2300°K, having an activation energy of under 8 kcal./mole at all flow velocities.
- (4) The type of carbon affected the reaction rate only slightly.

Result (1) is an important finding for it extends considerably the work of Meyer,⁶ Parker & Hottel⁴ and Gulbransen & Andrew.⁸ In the present work, it has been shown that under normal pressure, high temperature and high gas-velocity conditions, the combustion rate is first-order with respect to the partial pressure of oxygen in the *ambient* entering gas stream.

Results (2), (3) and (4) would normally be explained on the basis that the combustion rate was controlled primarily by the rate of mass transport of reactant to the carbon surface. Before agreeing to this conclusion in the present case, however, several facts should be brought out.

(a) As is seen in Table VII, the apparent activation energy for the combustion of petroleum-coke decreased with increase in gas injection velocity.

(b) Calculations of film thickness indicate that the film thickness at the high-gas velocities used are appreciably less than those required for the reaction to be entirely mass-transport controlled.

Considering (a), Kuchta *et al.*,⁷ among others, have shown from theoretical calculations that the reaction temperature of the carbon should have a negligible effect on the combustion rate of carbon when the reaction is diffusional (mass-transport) controlled. This means that the activation energy determined over such a temperature range should be negligible. On the other hand, in low-temperature experiments, i.e. at 500°, where there was no doubt that the combustion rate of carbon was controlled by its chemical reactivity, Gulbransen & Andrew⁸ determined an apparent activation energy for carbon combustion of 37 kcal./mole. Therefore, if in the present case the combustion rate of carbon were solely diffusion controlled, an increase in gas injection velocity should decrease the contribution of the diffusion-resistance to the

over-all resistance controlling combustion rate. This in turn should make the chemical resistance more important and increase the over-all apparent activation energy of the reaction. Such was not found experimentally in the present work.

Considering (b), it is informative to compare qualitatively the film thickness that would result if the diffusion rate were assumed to be equal to the combustion rate, i.e., the reaction controlled by mass transfer across the gas film, with experimental values of film thickness. For this calculation, Sherwood's equation¹¹ for steady-state counterdiffusion of both components in a binary mixture was used¹². Calculations give film thicknesses of 0.013 cm. and 0.0077 cm., respectively, for gas injection velocities of 20,000 and 60,000 ft. per min.

Direct experimental evidence by van der Hegge Zijnen,¹³ who studied the effect of air velocity parallel to a plate on film thickness 150 cm. from the upstream edge of the plate, showed that the thickness of the laminar layer at a velocity of 4700 ft. per min. was only 0.018 cm. If this thickness is assumed to vary with velocity to the 0.5 power,⁷ the predicted thicknesses at 20,000 and 60,000 ft. per min. would be 0.009 and 0.005 cm., respectively, which are less than the thicknesses calculated assuming diffusional control. Considering the fact that added turbulence by impingement of the gas stream against the surface would be expected to decrease the film thickness still further, the conclusion would appear to be that the reaction is not solely controlled, at least, by diffusion.

III Effect of admixture of various gases with injected oxygen on carbon reaction rates and CO/CO₂ ratio

Introduction

An admixed gas can affect the rate of a heterogeneous reaction either by physical or chemical means. There are at least two major ways in which the diluent can physically affect a heterogeneous reaction. One, it can dilute the reacting gas and thereby decrease reaction rate by decreasing the number of collisions of the reacting gas with the surface per unit time. Two, changing the diluent can affect the heat capacity, viscosity, thermal conductivity of the reactant mixture and diffusion rate of the reacting gas to the carbon surface. These factors, in turn, can affect the combustion rate.

There are also at least two major ways by which a diluent can chemically affect a heterogeneous reaction. One, the admixed gas can be in competition with the reacting gas for adsorption on active sites, can build up on these active sites and poison the reaction. Two, the admixed gas can affect the rate of gas-phase reactions which occur between the products of the heterogeneous reaction and the reacting gas. This in turn can affect the reaction rate by changing the concentration of the reactant at the solid surface.

In the present paper, the effect of different admixed gases, as well as sodium carbonate addition, on the combustion rates of carbon with oxygen and the CO/CO₂ ratios produced therefrom, under high-temperature and high-velocity conditions was investigated. The apparatus and operating procedure have been described in Part I.

Results

Helium addition

If the reaction rate were controlled by mass-transfer across a relatively stagnant film surrounding the carbon surface, it is conceivable that a change in the diluent gas from nitrogen to helium, and its attendant effect on increasing the rate of mass transport of the reacting gas to the carbon surface would increase the combustion rate. The results of two experiments, in which 4 and 10% by volume of helium in oxygen were used at an injection velocity of 20,000 ft. per min., are shown in Table IX. These results indicate that under these conditions the effect of changing the diluent from nitrogen to helium had an insignificant effect on reaction rate of petroleum-coke

Table IX

Comparison of helium with nitrogen as diluent for combustion of petroleum-coke rods

He, %	Temp., °K	CO/CO ₂ ratio	Carbon reacted, g. min. ⁻¹ cm. ⁻² %O ₂ ⁻¹
4.0	2066	4.1	1.98 × 10 ⁻²
10.0	2050	3.3	1.94
10% N ₂	2098	3.9	2.00

carbon. It is noted that the recorded carbon surface temperature for the run using nitrogen as a diluent is higher than those for helium. In line with the lower heat capacity of helium over nitrogen, it would be expected that at the same gas injection velocity the carbon reacted with the helium-oxygen mixture would have the higher surface temperature. Since the error in reading the surface temperatures was possibly greater than the temperature differences reported, however, probably no significance can be attached to this fact.

Carbon dioxide addition

It was desired to know whether carbon dioxide would be reduced under the temperature and velocity conditions of the experiments being reported. Accordingly, oxygen containing 10% carbon dioxide was reacted with petroleum-coke and lampblack carbons. The results of these experiments are shown in Table X in comparison with values for the corresponding temperatures, as taken from Part II. The CO/CO₂ ratios are calculated after correcting for the added carbon dioxide.

No appreciable change in the CO/CO₂ ratio is apparent and the reduction in the reaction rate is proportional to the added carbon dioxide. Therefore, under these conditions the CO₂ was not significantly reduced and acted only as a diluent.

Table X

Effect of carbon dioxide addition to inlet oxygen on CO/CO₂ ratio and combustion rate of petroleum-coke and lampblack rods

Carbon	CO ₂ , %	Temp. °K	CO/CO ₂ ratio	Carbon reacted, g. min. ⁻¹ cm. ⁻² %O ₂ ⁻¹
Petroleum-coke	10.3	2093	3.7	1.99 × 10 ⁻²
Petroleum-coke	—	2100	3.9	1.99
Lampblack	10.0	1955	14.8	2.14
Lampblack	—	1960	13.0	2.15

Carbon monoxide addition

A comparison of experiments with and without admixed carbon monoxide at a flow velocity of 20,000 ft. per min. on petroleum-coke carbon are shown in Table XI. The CO/CO₂ ratio is calculated after correcting for the added carbon monoxide. The results show that the carbon monoxide acted only as a diluent, the decrease in reaction rate being proportional to the amount of added carbon monoxide.

Table XI

Effect of carbon monoxide addition to inlet oxygen on CO/CO₂ ratio and combustion rate of petroleum-coke rods

CO, %	Temp., °K	CO/CO ₂ ratio	Carbon reacted, g. min. ⁻¹ cm. ⁻² %O ₂ ⁻¹
9.8	2030	2.5	1.91 × 10 ⁻²
—	2030	2.6	1.93
10.0	2070	3.4	2.01
—	2070	3.3	1.97

Water addition

Moisture was added to the oxygen stream by bubbling the oxygen through a 30-in. column of water contained in a 3-in. diameter lucite tube, 53 in. high. The moisture content of the oxygen, determined by adsorption, indicated almost complete saturation of the oxygen when passing through the saturator at the velocity used in these experiments. Table XII shows the results of a run at 20,000 ft. per min. on carbon from both petroleum-coke and lampblack, along with data for the appropriate temperatures taken from the figures for experiments in which no moisture was added.

Table XII

Effect of water addition to inlet oxygen on CO/CO₂ ratio and combustion rate of petroleum-coke and lampblack rods

Carbon	H ₂ O, %	Temp., °K	CO/CO ₂ ratio	Carbon reacted, g. min. ⁻¹ cm. ⁻² %O ₂ ⁻¹ 1.86 × 10 ⁻³
Petroleum-coke	1.89	2093	2.0	1.98
Petroleum-coke	0.04	2090	3.7	2.05
Lampblack	2.29	1965	5.3	2.15
Lampblack	0.04	1965	13.5	

The reaction rate was retarded slightly and the CO/CO₂ ratio was measurably reduced, especially for the lampblack, indicating the marked effect that moisture had on catalysing the oxidation of carbon monoxide. The gas-phase combustion of carbon monoxide has been shown by other workers^{14,15} to be markedly catalysed by water. It would be thought, however, that if the oxidation of carbon monoxide were occurring entirely in the gas phase the effect of water on changing the CO/CO₂ ratio for two different carbons would be similar. That this is not the case for the two carbons possibly could be attributed both to the differences in percentage of water in the gas and the carbon temperatures, as well as the nature of the carbon. Indeed, the decrease in reaction rates for the two carbons upon combustion with wet oxygen, as contrasted to dry oxygen, was almost identical, which would appear to rule out the possibility of the moisture affecting the surface reaction.

Chlorine addition

Arthur¹⁶ and Bridger¹⁷ have reported that carbon tetrachloride, phosphorus oxychloride and chlorine are capable of inhibiting the gas-phase oxidation of carbon monoxide. Arthur¹⁸ reported that phosphorus oxychloride also affects the combustion rate of artificial graphite.

Chlorine was added to the oxygen in the present work to investigate its effect on the combustion rate of petroleum-coke under high-velocity conditions. Initially 2% chlorine was added to the oxygen. When this amount of chlorine was admitted to the system in which the injection velocity of oxygen was 20,000 ft. per min. and the carbon surface temperature was 2000°K, the reaction was, however, immediately extinguished. In fact, it was found that 0.25% chlorine was sufficient to smother the reaction proceeding under the above conditions. When from 0.10 to 0.15% chlorine was admixed with the oxygen, several changes occurred. The surface temperature decreased as much as 280°, the CO/CO₂ ratio was tripled in some cases, the reaction rate decreased, and the reacting carbon surface assumed an entirely different appearance. The surface of the petroleum-coke carbon, resulting from the addition of chlorine to the injected oxygen, was very deeply eroded, consisting of jagged peaks and valleys and showing evidence of marked preferential reaction.

The results of the experiments with petroleum-coke in which chlorine was added are presented in Table XIII together with points taken at corresponding temperatures from Figs. 6 and 10 (see Part II) in which no chlorine was added. The reduction in reaction rate varied from 14 to 24%. This, together with the extinction of the reaction with slightly larger percentages of chlorine and the change in appearance of the carbon surface, strongly suggests that the carbon surface was being poisoned. The poisoning was not permanent, however, for after the chlorine was removed from the gas stream the system returned to its original condition. The return to normalcy did not occur as rapidly as the poisoning occurred, which was practically instantaneous, indicating

Table XIII

Effect of chlorine addition to inlet oxygen on CO/CO₂ ratio and combustion rate of petroleum-coke

Velocity, ft./min.	Chlorine, %	Surface temperature, °K	Temperature reduction, °C	CO/CO ₂ ratio	Carbon reacted, g. min. ⁻¹ cm. ⁻² %O ₂ ⁻¹ 1.03 × 10 ⁻³
10,000	trace	1910a	120	2.4	1.36
10,000	none	1910	—	1.3	1.59
20,000	0.11	1933a	160	4.6	1.84
20,000	none	1930	—	1.5	1.31
20,000	0.15	1777a	283	2.6	1.72
20,000	none	1780	—	0.8	1.89
30,000	0.11	2033a	117	5.0	2.33
30,000	none	2030	—	2.6	

a—Temperature before introduction of chlorine

that the poisoning agent was desorbed relatively slowly. It is possible that the chlorine was aided in its desorption by the action of the oxygen on adjacent points in the carbon body, thus weakening the forces holding the poisoning agent to the surface.

Table XIV

Effect of sodium carbonate addition to petroleum-coke rods on CO/CO₂ ratio and combustion rates

Na ₂ CO ₃ , %	Temperature, °K	CO/CO ₂ ratio	Carbon reacted g. min. ⁻¹ cm. ⁻² % O ₂ ⁻¹
2.0	2115°	3.7	1.90 × 10 ⁻²
0.0	2120	4.4	2.00
2.0	2000	2.1	1.80
0.0	2000	2.2	1.90

It is difficult to decide if the increase in the CO/CO₂ ratio was due chiefly to chlorine inhibition of the gas-phase oxidation of carbon monoxide or to preferential chemisorption of chlorine on carbon sites where production of carbon dioxide was originally predominant. By visual observation, the chlorine was undoubtedly affecting the reaction at the carbon surface. From the previous investigations of Arthur¹⁶ and Bridger,¹⁷ retardation of gas-phase oxidation would also be suspected.

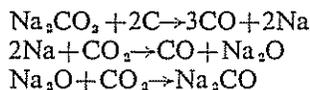
Sodium carbonate addition

Many inorganic materials have been added to carbon in an effort to influence the reactions that occur during combustion and gasification.^{19,20} Sodium carbonate has been found to exhibit a marked effect on combustion and, therefore, has received a large amount of attention. In the present work, sodium carbonate was added to the carbon rods to determine what effect, if any, it had on high-temperature, high-gas velocity combustion.

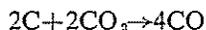
Petroleum-coke rods were impregnated with the carbonate by sealing them in a vessel which was then evacuated. A 15.5% solution of sodium carbonate was admitted to the vessel saturating the carbon rods. After drying in an oven at 105°, the increase in weight showed that 2% of the carbonate had been added to the rods.

The impregnated rods ignited very readily and the reaction proceeded smoothly thereafter. The change in the CO/CO₂ ratio between treated and untreated rods was within experimental error and the reaction velocity was decreased only slightly, as shown by the results in Table XIV, at an injection velocity of 20,000 ft. per min. The slight decrease in reaction rate, which is almost within experimental error, may be due to the decomposing sodium carbonate partially blanketing the carbon surface.

Fox & White,²¹ from experiments simulating a producer bed, postulated the action of sodium carbonate in the following mechanism :



the over-all reaction being



The fact that addition of sodium carbonate had no effect on the CO/CO₂ ratio probably is explained in the following manner. At the relatively high temperature of the surface, the carbonate is probably decomposed and evaporated from the carbon body before any appreciable reaction, according to the first step in the foregoing mechanism, can occur. Once the sodium atoms have left the surface they are rapidly swept away before further reaction with any carbon dioxide that may be present can take place in the gas phase, according to the other steps in the mechanism. This might also be taken as further indication that there is little, if any, homogeneous reaction occurring under these conditions.

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References

- ¹ Grodzovskii, M. K., & Chukhanov, Z. F., *Fuel, Lond.*, 1936, 15, 321
- ² Davis, H., & Hottel, H. C., *Industr. Engng Chem.*, 1934, 26, 889
- ³ Mayers, M. A., *Trans. Amer. Inst. min. (metall.) Engrs.*, 1938, 130, 408
- ⁴ Parker, A. S., & Hottel, H. C., *Industr. Engng Chem.*, 1936, 28, 1334
- ⁵ Smith, D. F., & Gudmundsen, A., *Industr. Engng Chem.*, 1931, 23, 277
- ⁶ Tu, C. M., Davis, H., & Hottel, H. C., *Industr. Engng Chem.*, 1934, 26, 749
- ⁷ Kuchta, J. M., Kant, A., & Damon, G. H., *Industr. Engng Chem.*, 1952, 44, 1559
- ⁸ Gulbransen, E. A., & Andrew, K. F., *Industr. Engng Chem.*, 1952, 44, 1034
- ⁹ Meyer, L., *Z. phys. Chem.*, 1932 (B)17, 385
- ¹⁰ Chukhanov, Z. F., & Karzhavina, N. S., *Fuel, Lond.*, 1941, 20, 73
- ¹¹ Sherwood, T. K., 'Absorption and Extraction', 1st edn., 1937, p. 9 (New York: McGraw-Hill Book Co., Inc.)
- ¹² Day, R. J., Ph.D. Thesis, The Pennsylvania State University, 1949
- ¹³ van der Hegge Zijnen, B. G., 'Measurements of the Velocity Distribution in the Boundary Layer along a Plane Surface', Thesis, Delft, 1924 (Delft: J. Waltman, jun.)
- ¹⁴ Fiock, E. F., & King, H. K., Nat. Advisory Commee., Aero. Tech. Rep. No. 531, 1935
- ¹⁵ Walker, P. L., jun., & Wright, C. C., *Fuel, Lond.*, 1952, 31, 37
- ¹⁶ Arthur, J. R., *Nature, Lond.*, 1946, 157, 732
- ¹⁷ Bridger, G. W., *Nature, Lond.*, 1946, 158, 236
- ¹⁸ Arthur, J. R., *Trans. Faraday Soc.*, 1951, 47, 164
- ¹⁹ Arthur, J. R., & Bowring, J. R., *J. Chim. phys.*, 1950, 47, 540
- ²⁰ Gulbransen, E. A., & Andrew, K. F., *Industr. Engng Chem.*, 1952, 44, 1048
- ²¹ Fox, D. Z., & White, A. H., *Industr. Engng Chem.*, 1931, 23, 259

Discussion

Dr. R. F. Strickland-Constable: I wish to comment on the general question of the temperature-dependence of the oxidation reactions of carbon in the technically useful range of temperatures from 1000° upwards. I have in the past carried out experiments with carbon filaments to determine the rates of reaction of O₂, CO₂, H₂O and N₂O¹⁻³ with carbon at temperatures between 900° and 2000°: gas pressures of the order of 0.05 mm. Hg were used in order to eliminate any influence of mass transfer in the gas phase on the observed rates, which were accordingly considered to correspond to true surface chemical reaction rates.

With oxygen, the rate of reaction at 900° was observed to be about the same as at 2000° with only slightly greater rates in between, so that roughly speaking the rate could be said to be temperature-independent over the great range of 900 to 2000°. Very similar results have since been obtained with oxygen by Duval⁴ whose observations confirmed my own in general outline, although differing in certain details.

In the case of CO₂, I found the reaction rate to be constant from 1400 up to 2000°. Similar results have since been obtained by Boulangier,⁵ who has studied the reaction in great detail: his region of constant temperature extended, however, only over the range 1100° to 1600°.

I found the rate of reaction with water vapour to be about the same at 1400° as at 2000°, with somewhat variable rates in between. Boulangier⁶ has found an approximately constant rate over the range 1200°–1700°. In my experiments with nitrous oxide the rate was approximately the same at 1100° as 1600°.

Summing up, therefore, it may be said that there is strong evidence that the rates of the reactions between carbon and oxidizing gases show the unusual feature of being largely temperature-independent over a considerable range between 1000° and 2000°.

In the paper of Day *et al.* experiments are described in which oxygen reacts with carbon at approximately atmospheric pressures: at the same time very high superficial oxygen velocities are used, in order, presumably, to reduce as far as possible the influence of mass transfer on over-all rate. Now in Fig. 13 of their paper, the curves for velocities of 40,000 and 60,000 ft./min. virtually coincide. The carbon consumption is therefore independent of gas velocity, and this

points to the conclusion that mass-transfer effects have been eliminated, and the true chemical surface-reaction rate is being observed. The authors appear, however, to hesitate to draw this conclusion on the grounds that the observed rate of reaction scarcely changes with temperature (as is clear from Fig. 13 where the curves are nearly horizontal), and this they consider a characteristic of reactions whose rates are mass-transfer-controlled. If, however, the conclusion drawn from the low-pressure experiments—that rate is independent of temperature—is correct, this argument of Day *et al.* is groundless, and they are entitled to regard their observed rates as true surface chemical reaction rates. Looking at the matter the other way round, it may in fact be legitimate to consider that Fig. 13 provides direct evidence that at high pressures also the chemical reaction rate is largely temperature-independent.

It may also be useful to compare the absolute values of the rates observed by myself at low pressures with those of the authors. Since the gas in the low-pressure experiments is at atmospheric temperature, only the filaments being at reaction temperature, it is safer to make the comparison on the basis of the collision yield, η , whose method of calculation will be given later. If the first-order reaction constant $k = 0.2 \text{ min.}^{-1}$ is taken from my results, Fig. 2,¹ the collision yield, η , can be calculated to be 30×10^{-5} . The authors' rate of carbon consumption would appear from their Fig. 9 to be about $2 \times 10^{-2} \text{ g. cm.}^{-2} \text{ min.}^{-1}$ for a pressure of 1 atmosphere, from which their η value would appear to be about 8.5×10^{-5} . In view of the nature of the comparison and the immense range of pressure extrapolation involved, the two figures must be considered to be in adequate agreement with each other, falling as they do within a factor of 4 of one another.

Reverting now to the oxidation with water, Graham *et al.* find rates of reaction represented by $\eta \rightarrow 2 \times 10^{-3}$. They then draw attention to the fact that in my low-pressure experiments η values of the order of 10^{-5} were observed, and that these values were confirmed by filament experiments carried out by Watt himself, and not yet reported in detail (page 320 above). They then suggest that this considerable difference, represented by a factor of 50, between low- and high-pressure results may be due to the fact that in the low-pressure experiments only the filament is at reaction temperature, the gas being virtually at room temperature. Whilst not wishing to deny that gas temperature *may* have some effect on the rate of reaction, I would like to suggest that a completely different explanation of the difference in rate is available. In my paper² two values of the rate of reaction with water at 1800° are given; in Table VII $k = 0.004$, whereas in Fig. 4 the values exceed 0.1. The difference is due to the state of the carbon filament itself: these filaments were coated with pyrolytic carbon at the beginning of each series of runs, and in this condition reacted extremely slowly with water: the runs of Table VII were with such a filament. Before the runs of Fig. 4 the filament was heated in 8 mm. of air for 8 min. at 1600°: this was a relatively large dose of oxidation and resulted in an increase in the reactivity of the filament to water at low pressures up to a value represented by $k = 0.1$; the treatment also resulted in a blackening of the originally silvery white surface of the filament. In other words, the rate of reaction of a given filament with water at these temperatures and pressures may vary by factors of hundreds or even thousands depending on the state of the carbon surface, which is itself largely determined by the pressure at which the carbon has previously been burnt. It seems entirely possible to believe that when carbon is burnt at atmospheric pressure the surface may be maintained in a state of reactivity much greater than that produced by very-low-pressure oxidation.

Furthermore, the k value shown in Fig. 4, at 2000°, namely, $\log_{10} k = 1.2$ or $k = 1.6 \text{ min.}^{-1}$, corresponds according to my calculations, to an η value of 1.8×10^{-4} , and this differs by a factor of 10, and not by a factor of 50 from the results of the high-pressure runs of Graham *et al.* who presumably took the value of $k = 0.004$ for their comparison. It is believed that a factor of 10 could quite easily be accounted for on the grounds of the differing states of the carbon surface: and in any case it is clear that absolute rates of reaction under such totally different conditions can only be compared with great caution, and a factor of 10 is probably scarcely significant. It is also to be noticed that the η values for filaments reacting with oxygen are some 4 times *greater* than those of Day *et al.* at atmospheric pressure: and in this connexion it must be emphasized that the rate of reaction of oxygen with the filaments was found to be largely independent of whether or not the filament had been subjected previously to high pressure oxidation.

The η values have been calculated from the first-order reaction constant, k , for the filament experiments by the formula

$$\eta = \frac{kV}{60aRT} / (2\pi RMT)^{-1}$$

where k is first-order reaction constant, min.^{-1}

a area of filament, cm.^2

V volume of reaction bulb, cm.^3

T temperature of reaction bulb, $^{\circ}\text{K}$

M molecular weight of gas

R gas constant, $\text{erg mole}^{-1} \text{ } ^{\circ}\text{K}^{-1}$.

The following very rough numerical values were used: $V = 1000$, $a = 1$, $T = 300$ (the reaction bulb, and hence the reacting gas, is at approximately room temperature).

References

- Strickland-Constable, R. F., *Trans. Faraday Soc.*, 1944, **40**, 333
- ² Strickland-Constable, R. F., *Trans. Faraday Soc.*, 1946, **43**, 769
- ³ Strickland-Constable, R. F., *Chem. & Ind.*, 1948, p. 771
- ⁴ Duval, X., Thèses, Université de Nancy, 1955 à 'Cinétique de la Combustion du Carbone Hautes Températures et Basses Pressions'; *J. Chim. phys.*, 1950, **47**, 339
- ⁶ Boulangier, F., Thèses, Université de Nancy, 1956: 'Cinétique des réactions d'oxydation du carbone par le gaz carbonique et de la vapeur d'eau à hautes températures et basses pressions.'

Prof. Walker: I agree with Dr. Constable that it is interesting to compare his low-pressure results with our high-pressure results on the carbon-oxygen reaction: I would, however, like to express my concern as to whether or not his experiments are in the region of chemical control, in the accepted sense. Dr. Constable's reasoning is that, at the low pressure which he is using, many more oxygen molecules are striking the surface per unit time than are reacting, and, therefore, the reaction cannot be in mass-transport control. I feel that the factor ignored is the low accommodation coefficient between the oxygen and carbon surface at low pressures. I think my point can best be made by quoting the abstract of the paper by Lothar Meyer on 'The Exchange of Energy Between a Hot Graphite Surface and Cold Gas Molecules,' presented at the 1957 Buffalo Carbon Conference:

'Hydrocarbons do not decompose on hot graphite surfaces up to 2300° if the gas pressure is so low that the mean free path of the gas molecules exceeds the dimensions of the vessel. This apparent paradox led to a detailed study of the exchange of energy between a cold gas molecule and the hot surface. The results can be summarized as follows: gas molecules reaching the surface are held by physical adsorption until they reach a critical temperature at which they evaporate. This critical temperature depends on the van der Waals' forces between the graphite and the gas molecule, but is essentially independent of the graphite temperature as long as the latter is higher than this critical temperature. Methane, e.g., evaporates at about 500° with graphite temperatures ranging from 850 to 1500° and methane temperatures between room temperature and 400°. The methane does not decompose during its contact with the hot graphite surface as it does not reach a temperature sufficiently high to cause decomposition before it evaporates.'

I am suggesting then that the factor determining the reaction rate is the temperature which the reacting species (oxygen, carbon dioxide, water, etc.) reaches before it leaves the surface. This temperature will determine the rate and amount of carbon-oxygen complex formed, which in turn will determine the reaction rate. If, as in the case of methane which Meyer quotes, this temperature is independent of the surface temperature, over a wide range, the reaction rate will also be independent of the surface temperature as Dr. Constable finds.

With regard to Dr. Constable's remarks regarding the low value for the reaction probability, η , reported by Graham *et al.*, I would like to express our views. The authors very nicely show that the magnitudes of the chemical and diffusion resistance terms are of about equal magnitude in their experiment. This clearly means that approximately half of the reaction is occurring on the external carbon surface and half on the interior of the carbon, instead of its occurring solely on the surface, as the authors assume.

Qualitatively, the key point is that ϵ , the reaction rate in g. of carbon reacted per cm.^2 per sec., is considerably too low. Therefore, when $1/\epsilon$ is plotted against $V^{-0.5}$ and extrapolated to zero, the C determined will be considerably too low. Since $C = 1/\eta n_0 \bar{c}$, this means that η will be considerably too high. Indeed, from surface-area work which we have done on samples in the intermediate zone of both chemical and diffusion control (Walker, jun., P. L., & Raats, B., *J. phys. Chem.*, 1956, **60**, 370), it appears that a reasonable area value would decrease η to approximately 10^{-5} , which the authors had expected.