

# THE COMBUSTION OF CARBON

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The rate of combustion of carbon under ordinary conditions is determined, not by the speed of the chemical reaction of oxygen and carbon, but by the rate at which oxygen can diffuse from the ambient atmosphere to the fuel surface. The rate of the primary surface reaction can be determined only under such conditions that the limiting effect of the diffusion process is removed. Such conditions are described in the first part of this paper in the discussion of experiments on combustion in oxygen at low pressures. The speed of the diffusion process itself may be determined from the measurements, described in the second part of the paper, of rates of combustion at ordinary furnace temperatures and pressures. The third part is a discussion of mathematical analyses of the entire process, in an attempt to express the rate of the reaction in terms of known physical quantities. It is to be noted that this paper does not consider two preliminary processes—the heating of the fuel and the expulsion of its volatile portion—which occur in industrial furnaces.

## I. EXPERIMENTS AT REDUCED PRESSURES

In order to determine the nature of the primary reaction between gaseous oxygen and a carbon surface, a succession of oxygen molecules should be permitted to impinge just once on a clean carbon surface, and the products should be removed from the sphere of reaction as soon as they are liberated. This ideal may be approached by the use of high vacuum technique.

In 1915 Langmuir (17) reported experiments on the oxidation of electrically heated carbon filaments suspended in evacuated bulbs cooled by liquid air. Provision was made for admitting gases to the bulb and for measuring the gas pressure by means of a McLeod gauge. With the filament at 950°C., carbon dioxide was the only product of combustion by oxygen, but as the temperature was increased, increasing amounts of carbon monoxide were formed. In order to recover all the oxygen, even as oxides of carbon, it was necessary to heat the filament to 2200°C. for half an hour, pumping continuously. When carbon dioxide was admitted to a filament at about 930°C., carbon monoxide was formed at the same rate at which

carbon dioxide disappeared. Evidently half of the oxygen remained in or on the carbon, in agreement with recent work of Broom and Travers (2).

Additional evidence that oxygen is very strongly held by clean carbon surfaces was supplied by sorption measurements on charcoal (18, 21). Only a small part of the oxygen admitted at room temperature can be removed by evacuation alone; it is necessary to raise the temperature while evacuating, when the oxygen comes off as oxides of carbon. The strength of the binding is indicated by measurements of the heat evolved in sorption (11, 14) which, for the first few increments of oxygen added, may be greater than the heat of combustion of carbon.

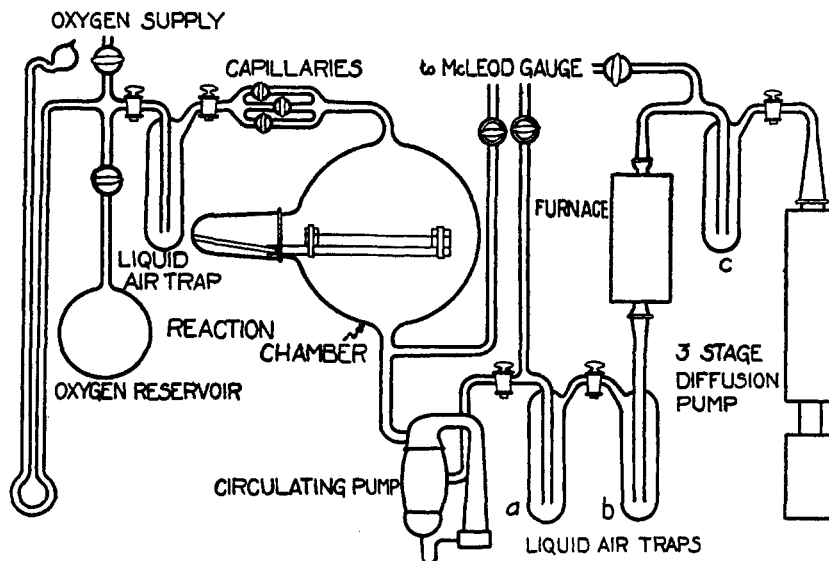


FIG. 1. DIAGRAMMATIC LAYOUT OF APPARATUS FOR LOW PRESSURE COMBUSTION OF CARBON

Quantitative measurements of the rate of combustion of graphite at oxygen pressures of the order of  $10^{-3}$  mm. of mercury were attempted by V. Sihvonen (27), using apparatus similar to Langmuir's but in which only a condenser tube sealed to the bulb was cooled with liquid air. The graphite sample was of measured size, and the reaction bulb contained a loop of platinum wire on which the carbon monoxide could be burned at the end of each run. Experiments were made with both flowing and static gaseous atmospheres, but both Sihvonen and Eucken, who also presented a discussion of the data (8), base their conclusions on the runs made with stationary atmospheres, although in this case secondary reaction is only partially prevented because of the presence in the atmosphere of a finite

concentration of carbon monoxide. Apparently because the technique was not sufficiently refined, the results of these experiments are not very consistent, but they agree in order of magnitude with those found later by L. Meyer (22), whose results show more clearly the relations among the variables.

Meyer reported results obtained in the apparatus shown diagrammatically in figure 1, in which oxygen at low pressures was passed at high velocity over the surface of electrically heated carbon filaments suspended between graphite blocks. The products of combustion were removed from the

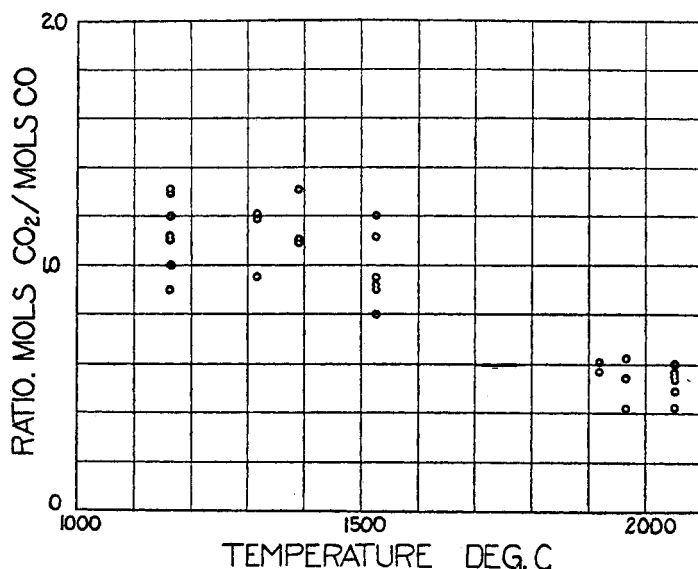


FIG. 2. LOW PRESSURE COMBUSTION OF CARBON

Ratio of carbon dioxide to carbon monoxide in products of reaction at various temperatures.

reaction chamber by a mercury diffusion pump, carbon dioxide was frozen out in the liquid air trap *a*, carbon monoxide was oxidized in a furnace containing palladized asbestos and removed from the gas stream by freezing in the traps *b* and *c*, and the remaining oxygen pumped out of the system by the three-stage mercury diffusion pump.

The pressure in the reaction chamber was about  $10^{-3}$  mm. of mercury, which allowed oxygen molecules a free path of the order of magnitude of the bulb diameter, while the high velocity permitted an average time in the reaction chamber long enough for about a hundred collisions. From these and other data the probable error due to secondary reaction was

estimated to be about 15 per cent. The method of gas analysis was found by blank runs to have an average error of about 7 per cent.

In the first runs ordinary carbon lamp filaments were used, but reproducible results could not be obtained unless they were built up by flashing them for 1 to 2 minutes at 2500°C. in an atmosphere of 1/3 methane and 2/3 hydrogen, thus producing uniform surfaces of graphite whose basal planes were found, by x-ray analysis, to be parallel to the filament axis. The treated filaments had the physical characteristics of exceptionally

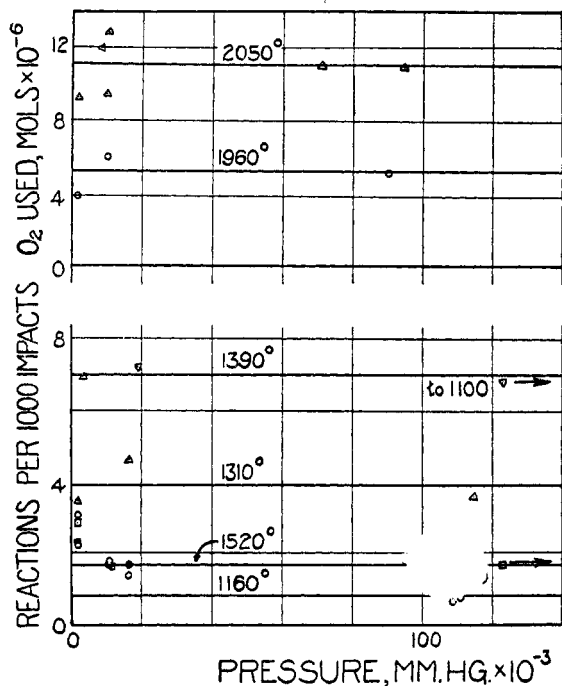


FIG. 3. LOW PRESSURE COMBUSTION OF CARBON

Rate of the reaction at various pressures in two temperature ranges. Numbers on lines indicate temperatures in degrees C.

pure samples of graphite, and could be used for three or four runs before pitting due to the combustion reaction made them useless.

The results of the experiments are given in figure 2, in which the ratio of the two products of reaction is plotted against temperature, and in figure 3, in which the rate of use of oxygen is plotted against pressure. It will be noticed that the results fall into two temperature groups, with a transition between 1450°C. and 1650°C. In the low temperature group, the ratio  $\text{CO}_2/\text{CO}$  is approximately constant within the limits of ex-

perimental error at about 1, as shown by figure 2, while, as is shown by the lower part of figure 3, in this temperature range the rate of reaction is proportional to the number of impingements of molecules on the carbon surface, i.e., to the gas pressure. The temperature coefficient of this reaction corresponds to an energy of activation of 20 to 30 kilocalories. In the higher temperature range, the ratio  $\text{CO}_2/\text{CO}$  is only about 0.5, while the rate of use of oxygen, plotted in the upper part of figure 3, is independent of the pressure.

Sorption measurements throughout the temperature range indicated that appreciable sorption occurred only in the low temperature region, where the amount of oxygen sorbed at any temperature was proportional

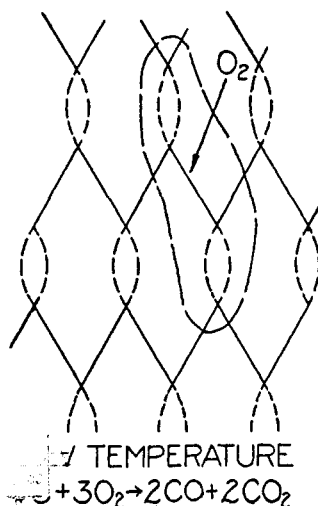
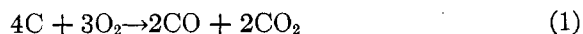


FIG. 4. MECHANISM OF COMBUSTION ACCORDING TO L. MEYER

Apices of hexagons represent carbon atoms; dotted lines represent adsorbed oxygen atoms;  $\text{O}_2$  with arrow represents oxygen molecule impinging from gas phase, when section within dashed lines breaks away from solid phase forming  $2\text{CO} + 2\text{CO}_2$ .

to the pressure, and the amount sorbed at any pressure fell off with increasing temperature. All of this sorbed oxygen could be removed by evacuation, in distinction to the fixation found by Langmuir, but it was not stated whether the oxygen came off as such or as oxides of carbon. The electrical resistance of the filaments was found to vary slightly with oxygen content. These results were interpreted as evidence that oxygen was able to penetrate the graphite lattice at temperatures below  $1500^\circ\text{C}$ .

Meyer suggested that the mechanism of oxidation at temperatures below  $1450^\circ\text{C}$ . is represented by the equation



while above this temperature, it may be expressed by



From the sorption measurements, and from the fact that hexagonal pits were etched in the filament surfaces, the conclusion was drawn that the low temperature reaction attacks the basal planes of the graphite lattice. Two molecules of oxygen are supposed to be sorbed on or dissolved in the lattice, possibly according to the scheme represented in figure 4, in which the apices of the hexagons represent carbon atoms and the dotted lines represent bound oxygen atoms. This sorption or solution causes an acti-

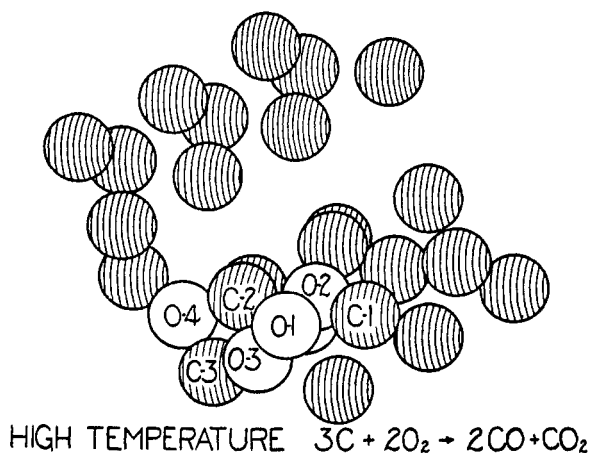


FIG. 5. MECHANISM OF COMBUSTION ACCORDING TO A. EUCKEN

Shaded spheres represent carbon atoms in hexagonal array extending indefinitely upward and to the right. Unshaded spheres represent oxygen atoms adsorbed on edges of the carbon lattice. In decomposing C-1 goes with O-2, C-2 with O-1 and O-4, and C-3 with O-3, giving  $2CO + CO_2$ .

vation of a region so that when a molecule of oxygen from the gas space impinges on this region four carbon atoms with their sorbed oxygen react according to equation 1. Above about  $1250^\circ\text{C}$ . the sorption of oxygen necessary for this reaction begins to fall off, until above  $1450^\circ\text{C}$ . it can no longer occur and the second type of reaction takes its place. For the latter, Meyer adopted the interpretation offered by Eucken (8) in connection with Sihvonen's experiments. The reaction was assumed to occur through the sorption of oxygen on the few very active spaces in the neighborhood of corner and edge atoms of the lattice, as shown in figure 5. The zero order of the reaction was explained by the large energy of binding of oxygen on these active spaces, since it would necessitate an average

life of sorbed molecules considerably greater than the time between collisions. The temperature coefficient indicates an activation energy for the high temperature reaction of the order of 90 kilocalories, which is of the same order of magnitude as the heat of sorption of the first increments of oxygen admitted to a clean carbon surface (11, 14).

More recently, Sihvonen has given a lengthy, largely theoretical discussion (28) of possible reactions of oxygen on graphite surfaces. While he agrees with Meyer in believing that some sort of specific binding of oxygen with solid carbon exists, he does not consider that the reaction represented by equation 1 is of as great importance as that represented by equation 2. His discussion does not involve so limited a mechanical picture as does Meyer's, and may be more generally acceptable.

The low pressure experiments described above make the conclusion inevitable that the combustion of carbon by gaseous oxygen at high temperatures involves the fixing of oxygen in some strongly held complex, which then breaks down to the two gaseous oxides. Although the experimental evidence is not yet unambiguous on this point, there is some reason for believing that the complex may be regarded as an intermediate compound whose decomposition produces the gaseous oxides in fixed proportions.

## II. EXPERIMENTS AT NORMAL PRESSURES

Early workers (7, 10, 16) on combustion conducted experiments at atmospheric pressures and at low temperatures, usually below 500°C. Rhead and Wheeler (25) circulated air or oxygen through a bed of charcoal which had previously been cleaned up by evacuation at high temperature. Their results showed that the first oxygen admitted does not immediately appear as gaseous oxides, that both carbon dioxide and carbon monoxide appear in the products of combustion at all temperatures, with increasing percentages of carbon monoxide as the temperature is raised, and that carbon monoxide is formed faster than it could have been liberated by the reduction of carbon dioxide. These data led them to the earliest expression of the theory of the formation of a strongly held oxide layer, to which they gave the general formula  $C_xO_y$ , as a necessary step in the combustion of carbon.

Various empirical indications of the speed of this reaction on different forms of carbon have been used for routine determinations of the combustibility of cokes. In all of these tests a standard amount of powdered coke is heated in a stream of air or oxygen and the combustibility measured by determining the ignition point (1, 3, 24), or determining the amount of carbon dioxide formed at a given temperature (6, 15). These tests give some sort of comparison of the speed of the surface reaction of oxygen on carbon, but the values obtained depend on the geometry of the apparatus, and are not suitable for calculations of the kinetics of the process.

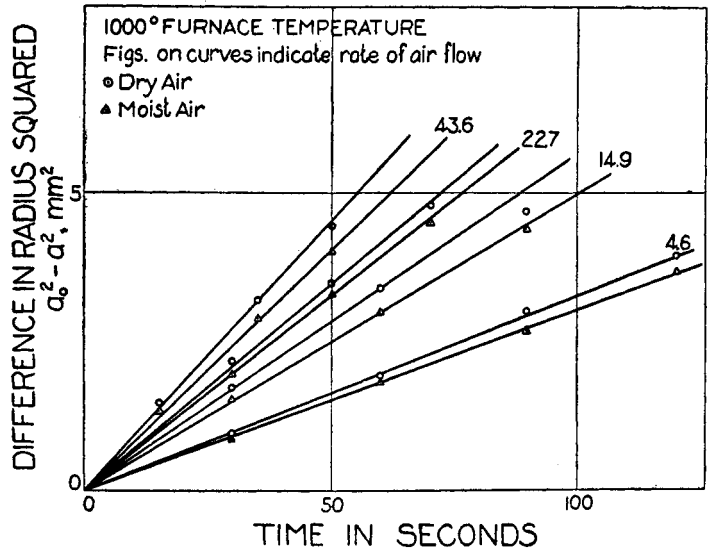


FIG. 6. PROGRESS OF COMBUSTION AT VARIOUS GAS VELOCITIES AT 1000°C.  
 (Smith and Gudmundsen)

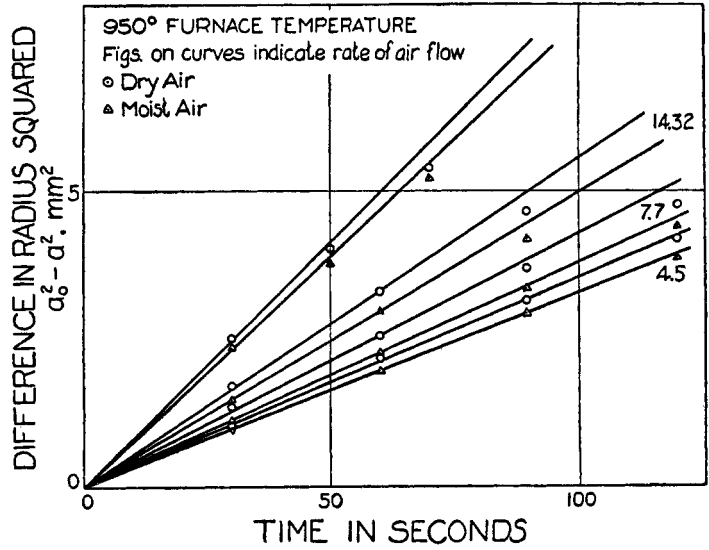


FIG. 7. PROGRESS OF COMBUSTION AT VARIOUS GAS VELOCITIES AT 950°C.  
 (Smith and Gudmundsen)



The later experimental work, stimulated by the increasing industrial use of pulverized fuel, was concerned with the determination of combustion rates under conditions approximating those of commercial furnace practice. Under these conditions the fuel temperature is so high that the rate of the chemical reaction at the fuel surface is very great and the speed of combustion is limited by the much slower rate of diffusion of oxygen to the fuel. Griffin, Adams, and Smith (12) arranged to photograph, on moving film, particles of pulverized fuel, of sieve sizes through 45 on 50 mesh, and through 80 on 90 mesh, as they fell through a vertical furnace open to the atmosphere. They assumed that the time of combustion was coincident

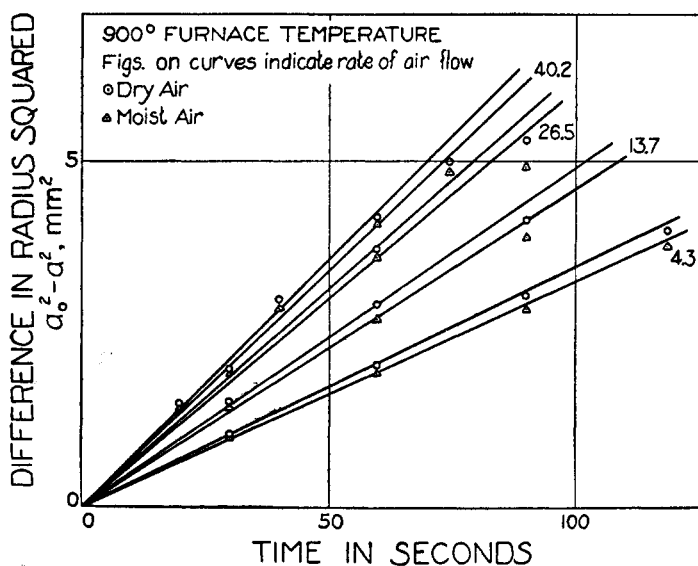


FIG. 8. PROGRESS OF COMBUSTION AT VARIOUS GAS VELOCITIES AT 900°C.  
 (Smith and Gudmundsen)

with the period of incandescence of a fuel particle, but, as the results determined on this basis are very erratic and the time of combustion of a given size of particle was found to increase greatly with furnace temperature, a result which disagrees with later experiments (29), this assumption is probably not justified.

Subsequently, spheres of electrode carbon, 4.6 mm. in diameter, were burnt in flowing air by Smith and Gudmundsen (29). Arrangements were made to follow the course of combustion by quenching the sample in nitrogen after definite periods of time, and weighing; and to follow the temperature of the sample surface during the burning by the use of an optical pyrom-

eter. Experiments were made using both wet and dry air, at furnace temperatures of 900°, 950° and 1000°C., and with gas velocities ranging from 1.09 to 10.25 ft. per second measured at 24°C. The particle sizes and air velocities used make the data applicable to the case of lump coal burning on a grate, but are too great for the conditions of pulverized fuel firing. Smith and Gudmundsen presented their results in terms of the "specific reaction rate,"  $k_s$ , in milligrams of carbon burnt per second per square millimeter of surface, but the data have been recalculated for this paper to give

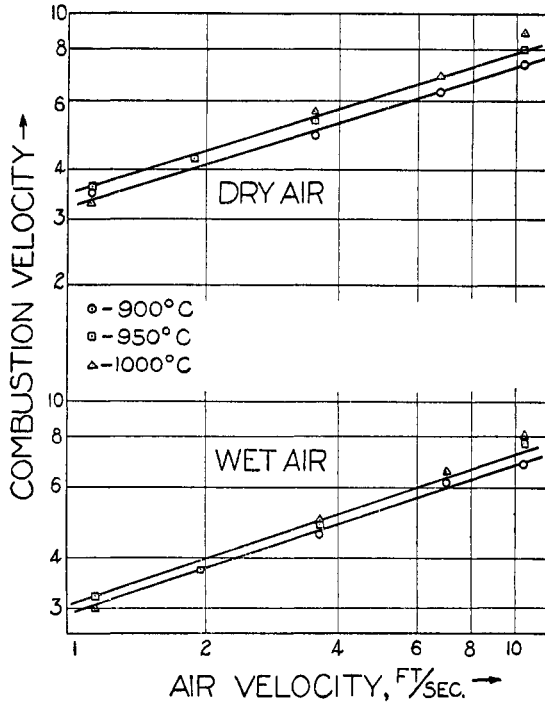


FIG. 9. VARIATION OF COMBUSTION RATE WITH GAS VELOCITY

figures 6, 7, and 8, in which the decrease in the square of the radius of the sample is plotted against the time of burning. The slopes of these curves give the combustion rate at unit radius. These may be plotted against the gas velocity on logarithmic scales as in figure 9, giving approximately straight parallel lines with a slope of 0.4. The effect of temperature on the combustion rate can not be determined from these experiments, since no consistent relation between the variables appears when they are plotted as in figure 10.

C. M. Tu (30) determined rates of combustion by weighing continuously

on a recording balance 1-inch diameter electrode carbon spheres suspended in a furnace through which were passed air and other oxygen–nitrogen mixtures at various rates of flow. In these experiments the spheres were not much reduced in size, so the variation of combustion rate with radius is not apparent. The rates of combustion, which were reported as the specific reaction rate,  $k_s$ , were directly proportional to the oxygen pressure. The values of  $k_s$  for air are plotted to logarithmic scales against velocity in figure 11. The slope of the high temperature curves has the value 0.42,

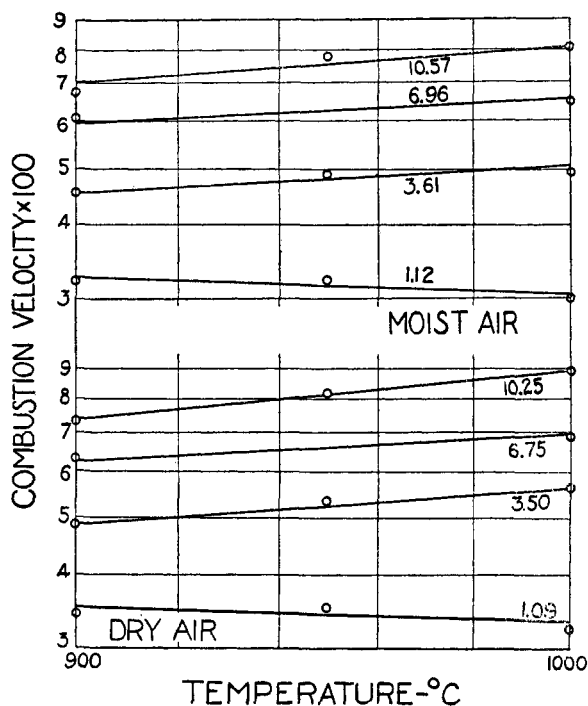


FIG. 10. VARIATION OF COMBUSTION RATE WITH TEMPERATURE

in close agreement with the slope found for the combustion rate–velocity curves representing Smith and Gudmundsen's data. In figure 12 the combustion rates are plotted against temperature, the numbers on the curves giving the velocity of air flow past the sample. Tu pointed out that the shape of these curves suggests that the combustion process consists of two types of action, the surface reaction and diffusion, in series, and that the over-all speed of combustion is determined by the slower. In the low temperature region the combustion rate has a temperature coefficient such that when  $\log k_s$  is plotted against  $1/T$  as in figure 13 a straight line is ob-

tained corresponding to an activation energy of about 35 kilocalories, a value not very different from that found by Meyer (22) for the surface reaction. Such a large temperature coefficient is characteristic of a chemical reaction, which, evidently, is slow enough in this region to permit oxygen to diffuse to the surface as fast as it is used without a great lowering of its partial pressure. As the temperature is increased the speed of chemical reaction increases, reducing the pressure of the oxygen at the fuel surface and increasing the concentration gradient, so that the rate of

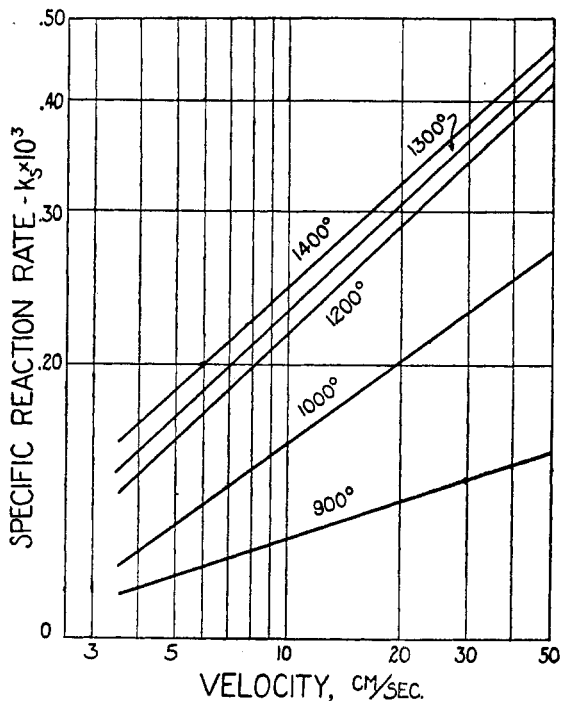


FIG. 11. VARIATION OF COMBUSTION RATE WITH GAS VELOCITY AT VARIOUS TEMPERATURES

(C. M. Tu)

diffusion becomes an increasingly important factor in determining the combustion speed. Figures 11 and 12 show that, in the high temperature range, the combustion rate has a small temperature coefficient and a large velocity coefficient, in agreement with the characteristics to be expected of such a physical process as diffusion.

### III. ANALYSIS OF THE COMBUSTION PROCESS

Several workers (4a, 4b, 5, 19, 23, 30) have calculated rates of combustion on the assumption that the rate of diffusion of oxygen to the carbon

surface and of the products of combustion away from it governed the speed of the process. For this purpose it must be assumed, first, that at any time the coördinates have the values they would reach if a steady state existed, even though the boundary condition changes with time; and, second, that the rate of reaction of oxygen with a carbon surface under the conditions of combustion is great enough to reduce the partial pressure of oxygen at the fuel surface considerably below that in the atmosphere at a distance from the surface. The fundamental differential equation amounts

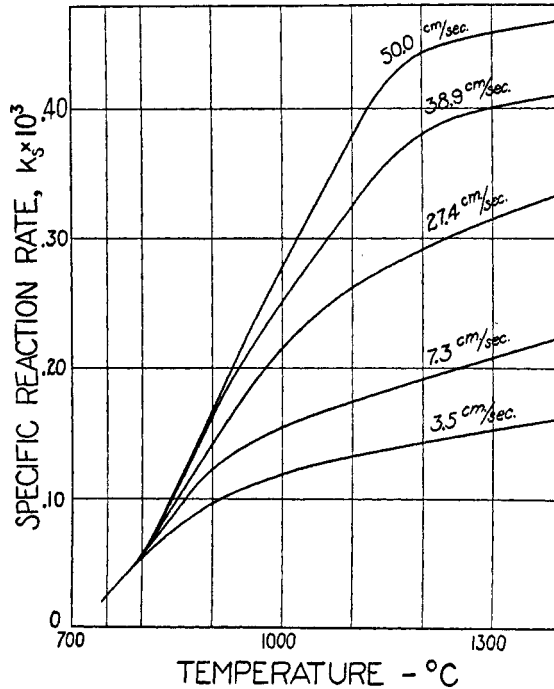


FIG. 12. COMBUSTION RATES AT VARIOUS TEMPERATURES AND GAS VELOCITIES  
(C. M. Tu)

to the statement that the increase in any constituent by flow or diffusion through the boundaries of an infinitesimal element of volume is exactly balanced by the decrease of that constituent by reaction within the volume element. That is,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ \frac{r^2}{RT} \left( D_i \frac{\partial p_i}{\partial r} + p_i V_r \right) \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[ \frac{\sin \theta}{RT} \left( D_i \frac{\partial p_i}{\partial \theta} + r p_i V_\theta \right) \right] = - A_i f(p_1, p_2, p_3, T) \quad i = 1, 2, 3 \quad (3)$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( k \frac{\partial T}{\partial r} + \frac{pc_p}{R} V_r \right) \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \left( k \frac{\partial T}{\partial \theta} + r \frac{pc_p}{R} V_\theta \right) \right] = -Hf(p_1, p_2, p_3, T) \quad (4)$$

where  $r, \theta$  = usual spherical coördinates.

$p_i$  = partial pressures of oxygen, carbon dioxide, and carbon monoxide, when  $i = 1, 2,$  and  $3,$  respectively.

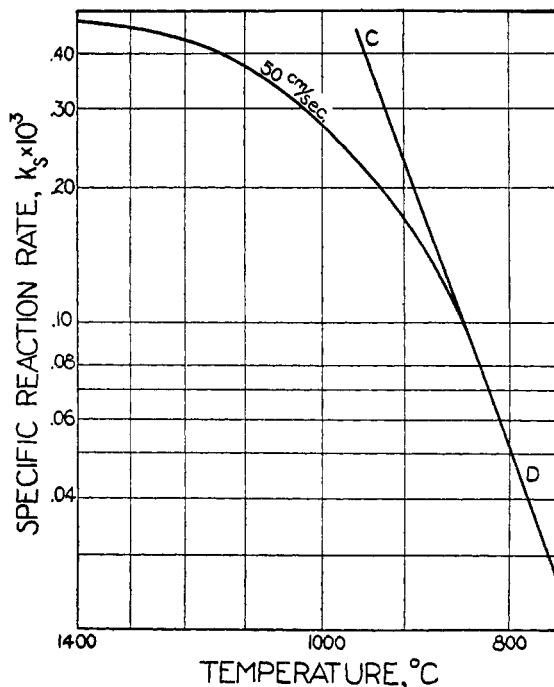


FIG. 13. EFFECT OF TEMPERATURE ON REACTION RATE

Line CD, coincident with experimental curve below 850°C., corresponds to activation energy of 35 kilocalories. Departure of experimental line from CD above 850°C. indicates effect of diffusion.

$T$  = absolute temperature.

$D_i$  = coefficient of diffusion associated with particular gas under discussion.

$V_{r,\theta}$  = components of gas velocity.

$f$  = function expressing the dependence of the rate of the homogeneous reaction on the concentration of the reactants and the temperature.

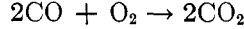
$k$  = coefficient of thermal conductivity of the gas.

$c_p$  = specific heat at constant pressure of the gas mixture.

$H$  = heat of the homogeneous reaction.

$A_{CO} = -A_{CO_2} = 1, A_{O_2} = \frac{1}{2}$  = molar ratios in which the constituents enter the homogeneous reaction.

This equation has not yet been solved, not only because of its complexity, but also because of the uncertainties of the form of "f," the expression for the unknown rate of the non-explosive homogeneous reaction:



and of the character of the flow of the atmosphere about a burning particle which determines the "V's." Nevertheless, it is possible to show that the rate of combustion is given by the rate of diffusion through a surface surrounding a fuel particle at a great distance from it with the permissible assumption that "f," the rate of the homogeneous reaction, is finite only at small distances from the particle, and becomes very small everywhere else. For, adopting vector notation, equations 3 and 4 may be expressed as

$$\nabla \cdot \left[ \frac{1}{RT} (D_i \nabla p_i + p_i \mathbf{V}) \right] = -A_i f \quad (5)$$

$$\nabla \cdot \left[ k \nabla T + \frac{p c_p}{R} \mathbf{V} \right] = -H f \quad (6)$$

The rate of use of oxygen in the homogeneous reaction is given by

$$\int_{\tau} A_i f d\tau$$

where  $\tau$  represents the volume inside a large surface  $S$  which is everywhere distant from the fuel surface. Substituting its equal from equation 5 for  $A_i f$  we have, by Gauss' theorem,

$$\begin{aligned} - \int_{\tau} \nabla \cdot \left[ \frac{1}{RT} (D_i \nabla p_i + p_i \mathbf{V}) \right] d\tau &= - \int_S \frac{1}{RT} (D_i \nabla p_i + p_i \mathbf{V}) \cdot d\mathbf{S} \\ &+ \int_s \frac{1}{RT} (D_i \nabla p_i + p_i \mathbf{V}) \cdot d\mathbf{s} \end{aligned} \quad (7)$$

where  $\mathbf{s}$  represents a surface at an infinitesimal distance outside the fuel surface. Now, the boundary condition representing the rate of reaction of oxygen with the carbon surface is given by

$$- \int_s \frac{1}{RT} (D_i \nabla p_i + p_i \mathbf{V}) \cdot d\mathbf{s} \quad (8)$$

Hence the total rate of use of oxygen is given by the sum of equations 7 and 8 or

$$K_{O_2} = - \int_S \frac{1}{RT} (D_1 \nabla p_1 + p_1 \mathbf{V}) \cdot d\mathbf{S}$$

If  $S$  be taken as a sphere of radius  $B$ , where  $B$  is very large,  $V_r = V \cos \theta$  and  $T$  is constant everywhere on  $S$ . Since only diffusion or gas velocity along the normal to the surface make contributions to  $K_{O_2}$ , we have

$$\begin{aligned} K_{O_2} &= \int_0^\pi \frac{1}{RT} \left[ \left( D_1 \frac{\partial p_1}{\partial r} + p_1 V \cos \theta \right) 2\pi r^2 \right]_{r=B} \sin \theta \, d\theta \\ &= \frac{4\pi D_1}{RT} \left( r^2 \frac{\partial p_1}{\partial r} \right)_{r=B} + 2\pi \int_0^\pi [p_1 r^2 V]_{r=B} \cos \theta \sin \theta \, d\theta \end{aligned} \quad (9)$$

Since in most cases, the combustion of a single particle does not change appreciably the concentration of oxygen in the stream of gas flowing past it,  $p_1$  in the second integral is constant with respect to  $\theta$  and the integral vanishes since  $\int_0^\pi \cos \theta \sin \theta \, d\theta$  vanishes, whence

$$K_{O_2} = \frac{4\pi D_1}{RT} \left( r^2 \frac{\partial p_1}{\partial r} \right)_{r=B} \quad (10)$$

This conclusion is of enhanced importance since its experimental verification is possible; if the concentration gradient close to the combustible were required, it would not be.

The analysis given above does not eliminate the necessity of solving the differential equations, since this is necessary to obtain  $\left( r^2 \frac{\partial p}{\partial r} \right)_{r=B}$ . In the simplest possible case, assuming first, that there is no homogeneous reaction, i.e., that  $f = 0$  everywhere, and the carbon burns directly to carbon dioxide; second, that the surface reaction is so fast that the partial pressure of oxygen at the surface is sensibly zero; third, that there is no flow of gas about the fuel; and fourth, that the temperature is everywhere constant; the differential equations reduce to

$$\frac{d}{dr} \left( r^2 D \frac{dp}{dr} \right) = 0$$

whence

$$p = \frac{C_2}{r} + C_1$$



and, introducing the boundary conditions,

$$p = P_1 - \frac{aP_1}{r}$$

where  $P_1$  = partial pressure of oxygen in the ambient atmosphere and  $a$  = radius of the particle. Then the combustion rate, in grams of carbon, is

$$\begin{aligned} K &= 12 \left[ 4\pi \frac{D}{RT} \left( r^2 \frac{dp}{dr} \right) \right]_{r=\infty} \\ &= 12 \left[ 4\pi a \frac{D}{RT} P_1 \right] \end{aligned} \quad (11)$$

The temperature restriction may be removed by assuming that the coefficient of diffusion,  $D$ , and the thermal conductivity follow the laws

$$D = D_0 \left( \frac{T}{T_0} \right)^2 = D_1 T^2$$

where

$$D_1 = \frac{D_0}{T_0^2}$$

and

$$k = k_0 \left( \frac{T}{T_0} \right)^{1/2} = k_1 T^{1/2}$$

where

$$k_1 = \frac{k_0}{T_0^{1/2}}$$

where  $D_0, k_0$  = values of the constants at  $T_0$  = some arbitrary temperature. Then, by methods analogous to those used in obtaining equation 11

$$K = 12 \left[ 4\pi a \frac{D_1 P}{R} \frac{T_2 + T_1 + \sqrt{T_1 T_2}}{3} \right] \quad (12)$$

where, if it be assumed that the particle loses heat only by conduction through the gas about it,  $T_2$  is given by

$$T_2^{1/2} - T_1^{1/2} = \frac{D_1 P H_1}{2Rk_1} \quad (13)$$

whence the temperature of the particle does not vary with its radius; while, if it be assumed that the particle may lose heat by radiation as well as con-

duction, as for particles at the outside of a pulverized fuel flame and also in Smith and Gudmundsen's experiments,  $T_2$  is given by

$$\frac{T_2^4 - T_1^4}{T_2^{3/2} - T_1^{3/2}} = \frac{1}{4\pi\sigma a} \frac{D_1 P H_1}{3R(T_2^{1/2} - T_1^{1/2})} - \frac{2k_1}{3} \quad (14)$$

where  $H_1$  = molar heat of combustion of carbon and  $\sigma$  = radiation constant in the Maxwell-Boltzmann law.

It is to be noted that, whether variable temperature be considered or not, the rate of combustion is proportional to the partial pressure of the oxygen and to the radius of the fuel particle. The former result was verified experimentally by Tu, and the latter is confirmed by the work of Smith and Gudmundsen. The curves of figures 6, 7, and 8 may be expressed approximately by the equations

$$(a_0^2 - a^2) = \frac{M}{2\pi\epsilon} t \quad (15)$$

where  $t$  = time,

$\epsilon$  = density of the fuel,

$M$  = combustion rate constant, and

$a_0$  = radius of the particle at time zero.

Differentiating, and multiplying through by  $a$ , we have

$$-4\pi\epsilon a^2 \frac{da}{dt} = Ma$$

But the rate of combustion is the rate of decrease in weight of the particle, whence

$$K_{\text{obs.}} = -4\pi\epsilon a^2 \frac{da}{dt} = Ma \quad (16)$$

The correctness of the temperature dependence of the combustion rate given by equations 12, 13, and 14 is more difficult to evaluate. For the condition of no radiation,  $K$  varies with a power of  $T_1$  between 1 and  $\frac{1}{2}$ . Tu's experiments, which were so arranged as to approximate this condition, indicate that the combustion rate varies as the 0.42 power of the temperature, as indicated by figure 14. Tu's calculations, based on finite film theory, agreed well with this temperature dependence, giving  $T$  the exponent 0.37, represented by the slope of the line AB. When radiation occurs,  $K$ , as represented by equations 12 and 14, varies as a power of  $T_1$  slightly greater than 1, which is in agreement with the somewhat inconsistent results of Gudmundsen and Smith shown in figure 10.

Burke and Schumann (4a, 4b, 5) and Tu (30) attempted to remove the

restriction of zero gas velocity by considering the particle to be surrounded by a finite film of stagnant gas whose thickness was calculated from Rice's formula (26) which was developed to account for the phenomena of heat transfer. While the existence of a stagnant fluid film is extremely doubtful (9, 13), the use of the concept for purposes of calculation has been fruitful in the field of heat transfer. Times of combustion calculated according to the method of Burke and Schumann (4b) have been plotted against the square of the particle radius in figure 15 for comparison with the data for dry

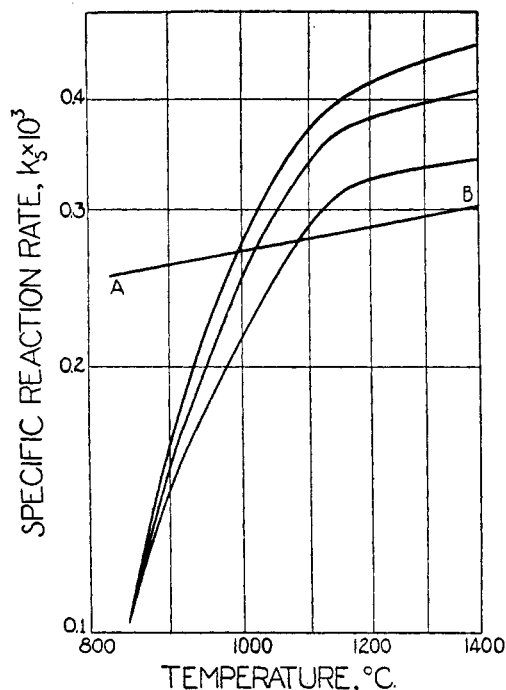


FIG. 14. EFFECT OF TEMPERATURES ON DIFFUSION RATE

Line AB corresponds to the temperature coefficient calculated for diffusion effect by C. M. Tu.

air in figure 6. The lines have a definite curvature, but this is in such a direction as to include the few points that fall off the straight lines of figure 6. If the deviations of those points from linearity are not due to experimental errors, the form of the Burke and Schumann equations, which give values of the combustion rate not exactly proportional to the radius for small particle sizes, is evidently more nearly correct, although the absolute values of the time of combustion are 60 per cent greater than those observed. This discrepancy may be due to the uncertainty of the values of diffusion

coefficients at the high temperatures involved, and of the correct values of the constants in the formula for the effective film thickness. In making similar calculations, Tu found it necessary to modify both the coefficient and the exponent of the Reynolds number in Rice's formula in order to obtain satisfactory agreement with his experimental data.

Burke and Schumann (5) also tried to remove the restriction concerning the homogeneous reaction by postulating the existence of a double film. In the outside film carbon dioxide diffused outward, while oxygen passed inward to the boundary of the inner film where it met and burned carbon monoxide diffusing out. The carbon monoxide was formed at the fuel surface by the reduction of carbon dioxide, which diffused inward through

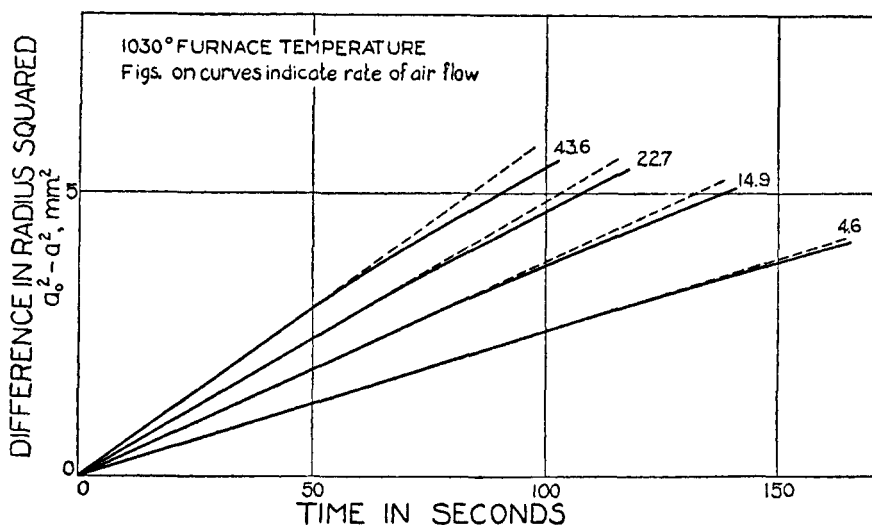


FIG. 15. PROGRESS OF COMBUSTION CALCULATED ACCORDING TO BURKE AND SCHUMANN  
Dotted lines are straight, corresponding to lines of figure 6

the inner film. This mechanism can not be accepted because of the fact that even if the partial pressure of carbon dioxide at the fuel surface were as great as that of oxygen in air, which is its maximum possible value, the rate of gasification of carbon, according to measurements (20) made in this laboratory, would be not more than 1/50 of the observed rates of combustion.

Indeed, the work of Meyer indicates that, even with oxygen, an appreciable pressure at the carbon surface may be required to account for observed rates of reaction. The maximum value of  $k$ , reported by Smith and Gudmundsen is in the neighborhood of 0.05 mg. of carbon burned per second per square millimeter at the highest air velocity with a furnace tempera-

ture of 1000°C., when the sample temperature was about 1530°C. At about this temperature, Meyer found a zero order reaction in which 0.047 mg. of carbon was burned per square centimeter per minute, a value only 1/6400 of that found at normal pressure. Two possibilities may account for this discrepancy. The reaction described by Meyer as of zero order may be of the first order; then, since the pressure at which the measurements were made was about  $10 \times 10^{-3}$  mm., a pressure of about 10 mm. would be required to bring the results into approximate accordance. On the other hand, Smith and Gudmundsen's temperature measurement may have determined not that of the particle surface, but the temperature of the flame of carbon monoxide formed by the primary reaction. In this case, if the surface temperature had been as low as 1250°C., the first order reaction described by Meyer could take place and a pressure of the order of 100 mm. would be required. This would certainly be great enough to invalidate the assumption of very small oxygen pressure at the fuel surface; and the rate of diffusion of oxygen and, hence, the combustion rate would not be proportional to the atmospheric oxygen pressure, but to the difference between that and the pressure at the fuel surface. However, in view of the agreement found between calculations based on previous assumptions and experimental data, it seems wise to suspend acceptance of the rates of the high vacuum oxidation until these are confirmed.

The foregoing discussion indicates that with the help of certain assumptions equations may be derived which, although they are rather unwieldy, give qualitative agreement with the effects of changes in the variables on the rate of combustion. Apparently because of uncertainties of the values of certain physical constants at the high temperatures involved, the agreement of the calculated rates with observed ones is only qualitative. This fact, combined with the uncertain validity of the assumptions involved in the derivation, justifies the use of an empirical formula based on the data discussed above and not in conflict with any theoretical considerations. This formula gives the rate of combustion, in milligrams of carbon per second, of a sphere in a high velocity stream of air at high temperature, as follows

$$K = 4\pi\epsilon a^2 \frac{da}{dt} = 0.068 \left( \frac{P_1}{0.21} \right) \left( \frac{T}{1273} \right)^n V^{0.4} a \quad (17)$$

In this expression  $P_1$  is to be measured in atmospheres,  $V$  is the air velocity in centimeters per second at normal temperature and pressure, and  $a$ , the radius of the particle, is to be measured in millimeters. The value of  $n$  is rather uncertain and may be between 1/2 and 3/2, although for many cases it is probably nearly equal to 1. The formula should be applied only

with reservations to the calculation of combustion rates under conditions differing greatly from those of the experiments of Smith and Gudmundsen.

#### CONCLUSIONS

Various experimental determinations of the mechanism and rate of combustion of solid carbon by gaseous oxygen have been reviewed, and previous mathematical analyses of the process have been discussed.

The nature of the primary reaction between graphitic carbon and oxygen has been considered on the basis of experiments made at such low gas pressures that diffusion effects were eliminated. These experiments have been shown to indicate that combustion involves the formation of a strongly held oxide or sorbed oxygen layer on the carbon surface. It has also been shown, however, that these high vacuum measurements of the rate of oxidation can not be brought into agreement even in order of magnitude with the rates determined at ordinary pressures.

It has been shown that, for ordinary industrial furnace conditions, the assumption that the rate of diffusion of oxygen to the fuel surface limits the speed of combustion, permits the calculation of combustion rates, which agree, both in order of magnitude and in the effect of changes in the variables, with observed rates. However, mathematical difficulties prevent a rational solution of the equations governing the process, so that the best expression that can be offered is the largely empirical one

$$K = 0.068 \left( \frac{P_1}{0.21} \right) \left( \frac{T}{1273} \right)^n V^{0.4a}$$

where the value of  $n$  is probably between  $1/2$  and  $3/2$ .

It may be concluded, then, that no complete formulation of the rates or mechanism of the combustion of carbon is yet possible. More experimental measurements at very low pressures are needed to resolve the discrepancy between the rates of the surface reaction already observed, and those known to occur in ordinary combustion. The experimental work at normal pressures must be extended over a much wider range of temperatures, pressures, sizes of combustible sample, and gas velocity—the latter especially toward the low velocity region to secure information concerning the conditions that govern powdered coal firing—and the work should be so arranged that constants required for the mathematical formulations may be secured. Last, a solution of an inhomogeneous differential equation of the second order is required before the experimental work can be expressed in its most complete form.

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