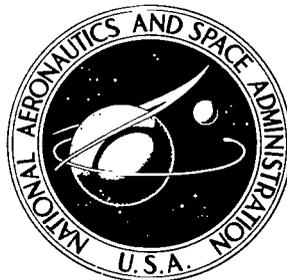


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OXIDATION OF CARBON
AT HIGH TEMPERATURES:
REACTION-RATE CONTROL
OR TRANSPORT CONTROL

by Howard G. Maabs
Langley Research Center
Hampton, Va. 23365

ERRATA

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By Howard G. Maahs

June 1971

Page 10: All values indicated on the ordinate of figure 2 should be multiplied by 10^{-2} .

Pages 7 and 15: The leading coefficient in the expression for k_T should read 1.51×10^5 instead of 1.51×10^{-5} . Figures 3 to 5, which are based in part on k_T , are correct as shown.

As an additional comment, it is recognized that the expressions for k_B and k_Z , also on pages 7 and 15, differ from those given in reference 10. However, these expressions on pages 7 and 15 were drawn from references 8 and 9 and are believed to be correct as shown; the slightly different expressions in reference 10 appear to be due to misprints.

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REACTION-RATE CONTROL OR TRANSPORT CONTROL

By Howard G. Maahs
Langley Research Center

SUMMARY

In spite of a general acceptance in making predictions of ablation rate that the oxidation rate of carbon is limited at temperatures of about 1650° K or above by the rate of oxygen transport to the carbon surface, a large body of existing experimental data on the carbon-oxygen reaction indicates that this may not be so. Furthermore, these data indicate a distinct departure from simple Arrhenius behavior and even a maximum in the rate curve as a function of temperature. These data have been analyzed and compared with theoretical maximum stagnation-point transport-limited rates. This comparison has shown that even at very high temperatures, in many situations the rate of chemical reaction is considerably below the theoretical maximum transport-limited rate. Hence, the carbon-oxygen reaction may be chemically controlled in many situations at much higher temperatures than previously suspected.

INTRODUCTION

There appears to be a general, unquestioned acceptance among investigators concerned with carbon or graphite as a material for high-temperature-reentry applications that the oxidation rate of carbon is limited at temperatures of about 1650° K or above by the rate of oxygen transport to the carbon surface. (See ref. 1.) While the concept of transport control of a gas-solid reaction is certainly theoretically sound, the assumption that all carbon-oxygen reactions (or even most of those of practical interest) are inevitably transport controlled above 1650° K is inconsistent with a considerable body of experimental data indicating the contrary. (See refs. 2 to 22.) For a situation of transport control to exist, it is a fundamental requirement that the chemical-reaction rate far exceed the oxygen-transport rate to the solid-carbon surface. Analysis of the previously cited experimental data suggests that often this is not true for many high-temperature situations of practical importance.

The purpose of this paper is to present a new analysis of the high-temperature oxidation rate of carbon for use as a material for reentry applications. The foundations of the present, generally accepted theory of the transport-controlled oxidation rate of carbon

at high temperatures will be briefly discussed, followed by an analysis of the previously cited experimental data. Finally, it will be shown that in many situations even at very high temperatures, the rate of chemical reaction does not even approach the theoretical maximum transport-limited rate, thereby demonstrating that the carbon-oxygen reaction may be chemically controlled in many situations at much higher temperatures than previously suspected.

SYMBOLS

C	constant
\dot{m}	mass-loss or reaction rate, g/cm ² sec
\dot{m}_D	theoretical maximum stagnation-point transport-limited mass-loss rate (eq. (7)), g/cm ² sec
p_a	air pressure, atm (1 atm = 101.3 kN/m ²)
p_{O_2}	oxygen pressure, atm
$p_{t,2}$	stagnation pressure of air adjacent to the surface, atm
R	gas constant, 1.987 cal/mole °K
r_n	nose radius, cm
\dot{s}	linear recession rate due to reaction, cm/sec
T	absolute temperature, °K

CURRENTLY ACCEPTED TRANSPORT-CONTROL THEORY

The present, generally accepted theory of transport control of the carbon-oxygen reaction at high temperatures is largely due to Scala (ref. 23). Two key features of the theory are the rate at which oxygen can be transported to the surface and the rate at which the chemical reaction is proceeding at the surface. To obtain an estimate of the chemical reaction rate at high temperatures, Scala reviewed the kinetic data and reaction-rate expressions presented by several authors. (See refs. 24 to 28.) Pertinent information from Scala's data sources is presented in table 1; reaction temperature and pressure

TABLE 1.- SUPPORTING DATA FOR KINETIC "BOUNDS" OF SCALA

Author	Reference	Range of supporting kinetic data		Reactant gas	Carbon studied	Kinetic expression presented by		Footnote
		T, °K	p _{O₂} , atm			Author	Scala (ref. 23)	
Gulbransen and Andrew	24, 29	698 to 848	0.002 to 0.13	O ₂	Spectroscopic grade; Ash, 0.02%; Density, 1.6 to 1.7 g/cm ³	$\dot{m} = 1.19 \times 10^2 e^{-36700/RT}$	$\dot{m} = 1.19 \times 10^2 e^{-36700/RT}$	(a)
Blyholder and Eyring	25	873 to 1073	0.0000013 to 0.0002	O ₂	Spectroscopic grade; Trace impurities; Density, 1.3 g/cm ³	$\dot{m} = C p_{O_2}^{1/2}$	$\dot{m} = 1.23 \times 10^2 e^{-42300/RT}$	(b)
Parker and Hottel	26	973 to 1373	0.002 to 0.20	Air	Brush carbon; Ash, 0.17%; Density, 1.55 g/cm ³	$\dot{m} = \frac{9.55 \times 10^6}{T^{1/2}} e^{-44000/RT} p_{O_2}$	$\dot{m} = \frac{9.55 \times 10^6}{T^{1/2}} e^{-44000/RT} p_{O_2}$	(c)
Frank-Kamenetskii	27	(d)	(d)	(d)	(d)	$\dot{m} = C e^{\frac{41100}{RT_0^2}(T-T_0)} p_{O_2}^m$	$\dot{m} = \frac{1.05 \times 10^{-3}}{T^{1/2}} e^{\frac{44000}{RT_0^2}(T-T_0)} p_{O_2}^{1/2}$	(d)
						where $T_0 = 1000^{\circ} \text{K}$; and $1/2 \leq m \leq 2/3$	where $T_0 = 1000^{\circ} \text{K}$	
Vulis	28	733 to 993	^e 0.21	Air	Welding carbon; Ash, 3.2%; Density, 1.5 g/cm ³	$\dot{s} = 5 \times 10^4 e^{-17500/RT}$	$\dot{m} = \frac{12.33}{T} e^{\frac{17720}{R} \left(\frac{1}{T^*} - \frac{1}{T} \right)} p_{O_2}$	(e)
						or $\dot{s} = 31.6 e^{\frac{17500}{R} \left(\frac{1}{T^*} - \frac{1}{T} \right)}$	where $T^* = 1240^{\circ} \text{K}$	
						where $T^* = 1240^{\circ} \text{K}$		

^aThe activation energy was obtained from reference 24 and the preexponential from reference 29; both are valid only at an oxygen pressure of 0.10 atm. In reference 24 the order of the reaction was shown to vary with pressure, being nearly first order above 0.13 atm, zero order between 0.002 atm and 0.02 atm, and intermediate order between 0.02 atm and 0.13 atm.

^bBlyholder and Eyring state that their data can be expressed with a constant activation energy of 42 300 cal/mole and a reaction order of one-half, but do not present a pre-exponential term. They further state that above 1073° K both the activation energy and the reaction order change. Scala's expression can be obtained by assuming an activation energy of 42 300 cal/mole and a zero-order reaction and by calculating a preexponential from data given in Blyholder and Eyring's paper at an oxygen pressure of 0.000034 atm.

^cParker and Hottel's data were obtained at low flow velocities where the reaction rate was dependent on flow velocity and, hence, was transport influenced. Accordingly, they carefully specified p_{O₂} in their kinetic expression to be the true oxygen pressure at the carbon surface. The carbon studied is described in reference 30.

^dFrank-Kamenetskii's rate expression is based on a reanalysis of Parker and Hottel's data (ref. 26). Frank-Kamenetskii concluded that the order of the reaction lay between one-half and two-thirds, with an activation energy of 41 100 cal/mole; however, no preexponential term was presented. Scala's expression can be reconstructed by assuming a reaction order of one-half and an activation energy of 44 000 cal/mole and by using a parameter from Frank-Kamenetskii's paper along with figure 6 of Parker and Hottel's paper to obtain a preexponential term. Use of this parameter accounts for the T^{1/2} appearing in the denominator of Scala's expression. It is interesting to note that the unconventional form of Frank-Kamenetskii's rate expression obscures the true meaning of the activation energy in the conventional sense.

^eAlthough Vulis conducted his experiments in air (test conditions are given in ref. 31), the test pressure is not stated and can only be assumed to be atmospheric. Vulis presented two rate expressions (which are virtually equivalent) but failed to specify a reaction order. The present author has not been able to reconstruct the rate expression presented by Scala, and the reason for its differing so markedly from those presented by Vulis is unknown. The high recession rates which are predicted by Vulis' expression, as well as the low reported activation energy of 17 500 cal/mole, can be attributed to catalytic accelerating effects from the very high concentration of impurities (3.2 percent ash) in Vulis' carbon samples. (See ref. 32.)

ranges, reactant gas, and carbon type, as well as the associated kinetic expressions are also included. It is observed that the kinetic expressions attributed by Scala to his sources differ in some instances from those which can actually be found in those sources. In order to permit engineering estimates of reaction rates from this diversity of kinetic expressions, it was necessary for Scala to arbitrarily select a kinetic form, a reaction order, a preexponential factor, and an activation energy which best bracketed the data. The resulting kinetic bounds (in the notation of the present report) were given by Scala in reference 23 as

$$\dot{m}_{\text{slow}} = 2.18 \times 10^4 e^{-42\,300/RT} p_{\text{O}_2}^{1/2} \quad (1)$$

$$\dot{m}_{\text{fast}} = 3.29 \times 10^8 e^{-44\,000/RT} p_{\text{O}_2}^{1/2} \quad (2)$$

which span a reaction-rate range of four orders of magnitude. Two major facts are to be noted regarding these kinetic expressions: first, they are admittedly arbitrary (ref. 23); and second, they are all based on data obtained below 1373° K.

Faced with the problem of estimating carbon-oxidation rates at higher temperatures, it has been customary for the engineer to extrapolate equations (1) and (2) linearly without regard to the temperature and pressure-range limitations of the data or to several cautionary statements concerning changing reaction order and activation energy given by the authors of the data. (See table 1 and refs. 24 to 32.) Although such extrapolation is convenient and often even necessary in the absence of more appropriate data, such extrapolation is without theoretical justification, particularly in the case of heterogeneous reactions. (See, for instance, refs. 11, 33, and others.) Rosner and Allendorf (refs. 16 and 18) have shown that linear extrapolation of simple Arrhenius expressions such as equations (1) and (2) will, at high temperatures, often lead to predicted oxidation-rate probabilities exceeding those theoretically possible (i.e., predictions of more than one carbon atom being removed from the surface per one oxygen atom colliding with the surface).

The reason a linear Arrhenius expression cannot be expected to adequately describe a gas-solid reaction is that there may be a large number of separate, competing kinetic steps involved (such as adsorption of the reactant, surface migration of the reactant to an active site, chemical combination with a carbon atom at that site, desorption of the product, etc.). Each of these steps may be of greater or lesser importance as the temperature or pressure is changed. Additional complicating kinetic steps are introduced if the reactant dissociates (as might oxygen, O₂), if multiple products are formed (as, for instance, carbon dioxide, CO₂, and carbon monoxide, CO), if an inert diluent in the reactant gas competes for active sites (as might nitrogen, N₂, in air), if there is more than one type of active site, and so forth. Since these kinetic steps are, in general, temperature and pressure dependent, both the apparent activation energy and reaction order of the

reaction may change as the temperature and pressure change. Therefore, although it is often possible, over a sufficiently narrow range of temperature and pressure, to correlate heterogeneous kinetic data by a simple Arrhenius expression, such an expression cannot be applied with reliability outside that range unless it is somehow known that the predominating kinetic mechanism is the same.

KINETIC EXPRESSIONS AT HIGH TEMPERATURES

A number of kinetic expressions have been developed (see refs. 2 and 8 to 11) from high-temperature kinetic data which make an extrapolation of equations (1) and (2) unnecessary. These kinetic expressions are based on data obtained at temperatures as high as 2773°K , but at experimental conditions such that reaction-rate limitations due to oxygen transport were absent. One such kinetic expression is that of Blyholder, Binford, and Eyring (ref. 2). It is based on low-pressure kinetic data taken by the hot-carbon-filament technique drawn from references 3 to 7. Figure 1 shows these data as adjusted by Blyholder et al. (ref. 2) to a common pressure of 10^{-2} torr oxygen ($1 \text{ torr} = 133.3 \text{ N/m}^2$).

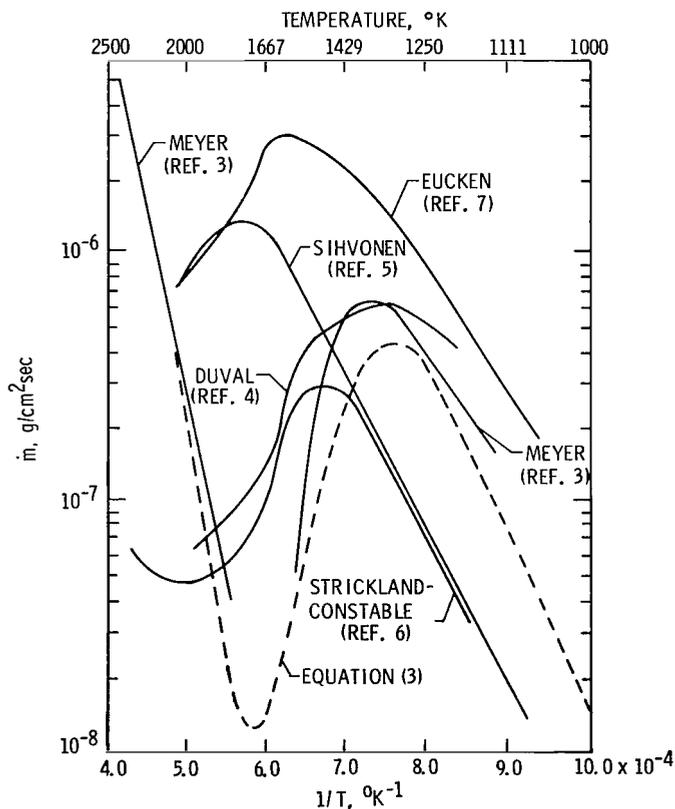


Figure 1.- Carbon filament-oxygen reaction at $p_{\text{O}_2} = 10^{-2}$ torr.
(After Blyholder, Binford, and Eyring (ref. 2).)

(Determining reaction rates at low pressures has the virtue that the low pressure effectively eliminates transport limitations by increasing the mean free path of the gaseous reactant. For instance, at an oxygen pressure of 10^{-2} torr and a temperature of 2000° K, the mean free path of molecular oxygen is on the order of 8 cm.) A most interesting aspect of the data in figure 1 is that, without exception, maxima exist in the various rate curves. In addition, the data of Meyer (ref. 3) and Strickland-Constable (ref. 6) show that as the temperature is increased beyond the rate maximum, a minimum is reached after which the rate increases again. It is unlikely that sublimation is responsible for this second increase in rate, since the theoretical free vaporization rate (i.e., the theoretical maximum vaporization rate) of carbon is only 4.6×10^{-10} g/cm²sec at 2000° K. (See ref. 34.) Quantitative differences in the data presented in figure 1 can be ascribed to differences in structural and chemical (i.e., impurities) properties of the various carbons employed (refs. 2 and 35) in addition to possible differences in experimental technique. The plot of the kinetic expression developed for these data by Blyholder et al. is shown in figure 1 as the dashed line. It may be given as

$$\dot{m} = 2.58 \times 10^{-7} k_1 f p_{O_2} + 3.4 \times 10^{-10} k_2 (1 - f) \quad (3)$$

where

$$k_1 = 1.6 \times 10^8 e^{-30\,000/RT}$$

$$k_2 = 2.2 \times 10^9 e^{-80\,000/RT}$$

$$k_3 = 4.2 \times 10^{24} e^{-175\,000/RT}$$

$$f = \frac{2k_2}{2k_2 + k_3}$$

The theoretical basis on which this equation was developed is that there are two types of reaction sites which are thermally convertible one into the other according to a first-order rate expression.

Another high-temperature kinetic expression is that of Strickland-Constable and coworkers (refs. 8 to 10) and is based on their data on the reaction rate of pyrolytic graphite. Experimentally, pyrolytic-graphite rods 4 mm on a face by 2 mm thick were electrically heated, and an unheated jet of oxygen or of oxygen-nitrogen mixtures was impinged on their surfaces at high velocities in the (impact) pressure range 0.20 to 0.23 atm oxygen. Rate maxima were observed at about 2173° K. Similar experiments conducted on lampblack carbon and reactor-grade graphite also showed rate maxima but at absolute rates about nine times faster than those for the pyrolytic graphite. In view of

this result, the very compelling argument was advanced (ref. 8) that since oxygen can obviously be transported to the pyrolytic-graphite surface nine times faster than the rate required to maintain its observed reaction rate, its reaction rate clearly cannot be transport limited. This conclusion was further substantiated by an independent experiment (ref. 9) in which the reaction rate of the pyrolytic graphite was studied as a function of jet velocity at the temperature of the rate maximum. At low jet velocities, the reaction rate increased with velocity; but above 2500 cm/sec, the rate leveled off, no longer increasing with velocity. However, at the same experimental conditions, the rate of reaction of a reactor-grade graphite continued to increase with increasing velocity. Hence, it could be safely concluded that the observed reaction rate of the pyrolytic graphite represented the true kinetic rate and was not influenced by transport limitations. A kinetic expression was developed in reference 8 for the pyrolytic-graphite data on the assumption that CO is the primary product of the reaction and that there are two types of active sites on the surface which undergo thermal interconvertibility. This kinetic expression may be given as¹

$$\dot{m} = \frac{12k_A k_B p_{O_2}^2}{(1 + k_Z p_{O_2})(k_T + k_B p_{O_2})} + \frac{12k_T k_B p_{O_2}}{k_T + k_B p_{O_2}} \quad (4)$$

where

$$k_A = 20e^{-30\,000/RT}$$

$$k_B = 4.46 \times 10^{-3} e^{-15\,200/RT}$$

$$k_T = 1.51 \times 10^5 e^{-97\,000/RT}$$

$$k_Z = 21.3e^{4100/RT}$$

This expression was further shown to be in good qualitative agreement with the earlier carbon-filament data of Strickland-Constable (ref. 6) at oxygen pressures of 2.5×10^{-5} atm and of Duval (ref. 4) at oxygen pressures of 10^{-6} atm.

Ong, in an impressive theoretical analysis (ref. 11), developed yet another kinetic expression valid at high temperatures. He applied the transition-state theory of kinetics to a deduced set of controlling kinetic steps, calculating the required transition energies by statistical thermodynamics, and evaluating several undetermined constants in his final expression from the data of Okada and Ikegawa (ref. 12). Ong's theoretical development

¹The expression originally given by Nagle and Strickland-Constable (ref. 8) contained a typographical error which was subsequently corrected in references 9 and 10.

(ref. 11) differs considerably from those of Blyholder et al. (ref. 2) and Strickland-Constable and coworkers (refs. 8 to 10) in that he assumed only one type of active site on the carbon surface. Another important feature of Ong's development is that he considered two product species from the carbon-oxygen reaction, CO₂ at low temperatures and CO at higher temperatures. Also, a rate maximum is predicted by Ong's kinetic expression, which he attributes to a change in the chemical potential of vibration of molecular oxygen. Ong's rate expression may be given as

$$\begin{aligned} \dot{m} = & F_{\text{CO}_2} e^{-22800/RT} \left[\frac{k_1 p_{\text{O}_2}}{1 + (k_1 k_3 p_{\text{O}_2})^{1/2} + k_1 p_{\text{O}_2}} \right] \\ & + 2F_{\text{CO}} e^{-51400/RT} \left[\frac{(k_1 k_3 p_{\text{O}_2})^{1/2}}{1 + (k_1 k_3 p_{\text{O}_2})^{1/2} + k_1 p_{\text{O}_2}} \right] \end{aligned} \quad (5)$$

where²

$$F_{\text{CO}_2} = 2.95$$

$$2F_{\text{CO}} = 9.5 \times 10^3$$

$$k_1 = e^{-(78410 - \mu_1)/RT}$$

$$k_3 = e^{-(5760 - \mu_3)/RT}$$

$$\mu_1 = RT \left\{ -\ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} kT \right] - \ln \left(\frac{T}{\sigma \theta_r} \right) - \ln(\omega_e) \right\}$$

$$\mu_3 = RT \left[\frac{\theta_v}{2T} + \ln \left(1 - e^{-\theta_v/T} \right) \right]$$

²Table 5 of Ong's paper (ref. 11) lists F_{CO_2} as 2.95×10^{10} and F_{CO} (instead of $2F_{\text{CO}}$) as 9.5×10^8 . These values are apparently in error when compared with figure 1 of his paper. The corrected values are shown above. In the expression for k_3 , Ong gives the constant in the exponent as -7990 cal/mole, however, the value of -5760 cal/mole has been chosen here because it gives better agreement with figures 4 and 5 of Ong's paper and also with the rate data of Okada and Ikegawa as shown in figure 1 of Ong's paper.

where

m = Molecular mass of oxygen

k = Boltzmann constant

h = Planck constant

$\sigma = 2$, a symmetry number

$\theta_r = 2.07^\circ \text{ K}$, characteristic temperature for rotation

$\omega_e = 3$, degeneracy of the electronic ground state

$\theta_v = 2230^\circ \text{ K}$, characteristic temperature for vibration

Since several constants in equation (5) were determined from the data of Okada and Ikegawa (ref. 12), it may be of interest to discuss briefly their experiment. Cylindrical specimens of artificial graphite, 10 mm in diameter, were heated electrically in room-temperature air at 1 atm with oxygen supplied only by natural convection. Surface temperatures were between 973° K and 2273° K , and Okada and Ikegawa assumed a transport-limited reaction. Although no experimental proof is given to support this assumption, it seems reasonable because of the experimental conditions. In view of this uncertainty, it is peculiar that Ong should have chosen these data for determining his kinetic constants. Nevertheless, it is interesting to note that whether or not the data are truly transport influenced, a very good representation of them can be obtained on the basis of theoretical considerations of reaction kinetics and statistical thermodynamics alone. It becomes apparent, then, that a nonlinear rate curve does not inevitably imply transport influence. This point has also been made by Rosner and coworker in references 18 and 19.

In addition to the three kinetic expressions already presented, a fourth expression can be formulated by employing a suggestion of Essenhigh (ref. 13) in discussing rate data obtained by Golovina and Khaustovich (ref. 14). These data are for 15-mm-diameter spheres reacted in oxygen-nitrogen mixtures of air composition (presumably at 1-atm total pressure) at flow velocities of 60 cm/sec. Essenhigh deduced that at these high velocities, oxygen transport should not significantly influence the reaction rate at the experimental conditions of Golovina and Khaustovich. (This is partially confirmed by other data presented by Golovina and Khaustovich showing that the rate of the carbon-carbon dioxide reaction is independent of gas velocity in the 20 cm/sec to 80 cm/sec velocity range.) Essenhigh proposed that the rate data might be adequately represented

in terms of a simple adsorption-desorption mechanism with desorption controlling at low temperatures and adsorption controlling at high temperatures. The activation energy of desorption was assumed to be on the order of 40 000 cal/mole, and the activation energy for adsorption was reasoned to lie in the range 1000 to 5000 cal/mole. Although Essenhigh did not compare this proposed mechanism with Golovina and Khaustovich's data, this comparison can be made easily. By taking the activation energy for adsorption to be 2000 cal/mole and by evaluating two undetermined constants from the data of Golovina and Khaustovich, a kinetic expression was developed

$$\dot{m} = \frac{k_1 k_2 p_{O_2}}{k_1 p_{O_2} + k_2} \quad (6)$$

where

$$k_1 = 5.48 \times 10^{-3} e^{-2000/RT}$$

$$k_2 = 5.21 \times 10^3 e^{-40\,000/RT}$$

Comparison of this expression with the data of Golovina and Khaustovich is shown in figure 2. Although this expression fairly satisfactorily represents the data, it suffers from the oversimplification that it does not adequately account for the change in product from CO₂ to CO as temperature increases, nor does it predict a rate maximum at high temperatures. What is important, however, is that a distinctly nonlinear rate curve (when plotted in an Arrhenius plane) can be adequately described by elementary considerations of heterogeneous kinetics without recourse to the concept of transport limitations.

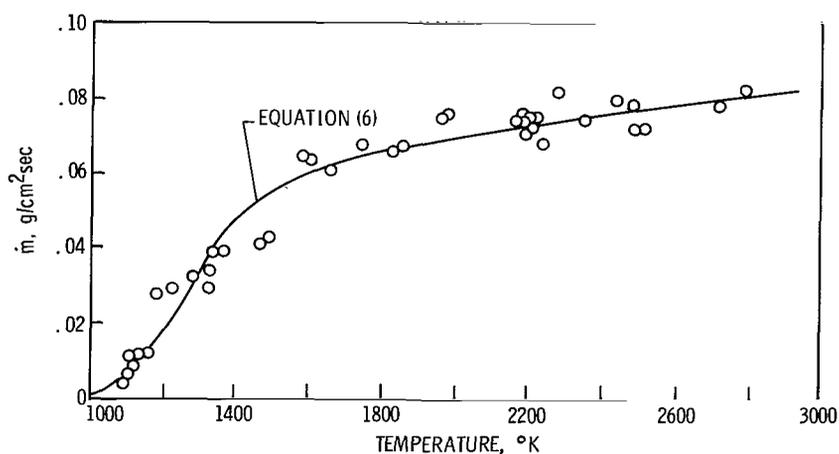


Figure 2.- Carbon sphere-air reaction. Data of Golovina and Khaustovich (ref. 14).

Equations (3) to (6) represent the only kinetic expressions which could be found or easily formulated from data in the literature. However, the literature also contains extensive additional data on the carbon-oxygen reaction at high temperatures further indicating distinctly nonlinear rate curves; these data are briefly discussed in appendix A.

For purposes of comparing the predictions of the several kinetic expressions (eqs. (3) to (6)), mass-loss rates have been calculated at air pressures of 0.01 atm, 1 atm, and 100 atm and are plotted in figures 3 to 5. The temperature and pressure ranges of the supporting data for these kinetic expressions are listed in table 2. For comparison, the predictions of Scala (ref. 23) "fast" and "slow" kinetic expressions (eqs. (1) and (2)) and predictions of theoretical maximum stagnation-point transport-limited rates, based on the expression

$$\dot{m}_D = 1.711 \times 10^{-2} \left(\frac{p_{t,2}}{r_n} \right)^{1/2} \quad (7)$$

from reference 23, for nose radii of 0.1, 1.0, 10, and 100 cm are also included in figures 3 to 5. From these figures, it is seen that at temperatures above about 1700° K, all four high-temperature-rate expressions predict rates one order of magnitude or more below a linear extrapolation of the "slow" rate expression, and five orders of magnitude or more below a linear extrapolation of the "fast" rate expression. (It is of interest to

TABLE 2. - KINETIC EXPRESSIONS

Author	Reference	Equation	Range of supporting kinetic data	
			T, °K	pO ₂ , atm
Scala ("slow")	23	1	698 to 1373	See table 1
Scala ("fast")	23	2	698 to 1373	See table 1
Blyholder et al.	2	3	1050 to 2300	^a 0.0000132
Strickland- Constable	8 to 10	4	1273 to 2673	^b 0.20 to 0.23
Ong	11	5	973 to 2273	0.21
Essenhigh (extended)	13	6	1073 to 2773	^c 0.21

^a Common pressure to which Blyholder et al. extrapolated data from various sources and at which they formulated their rate expression.

^b Impact pressure of the gas impinging on the carbon surface. The kinetic expression was, however, also qualitatively substantiated at 2.5×10^{-5} atm (refs. 8 and 10), and at 1×10^{-6} atm (ref. 10).

^c The test-gas composition was equivalent to air and, although not stated, the pressure may be presumed to be atmospheric.

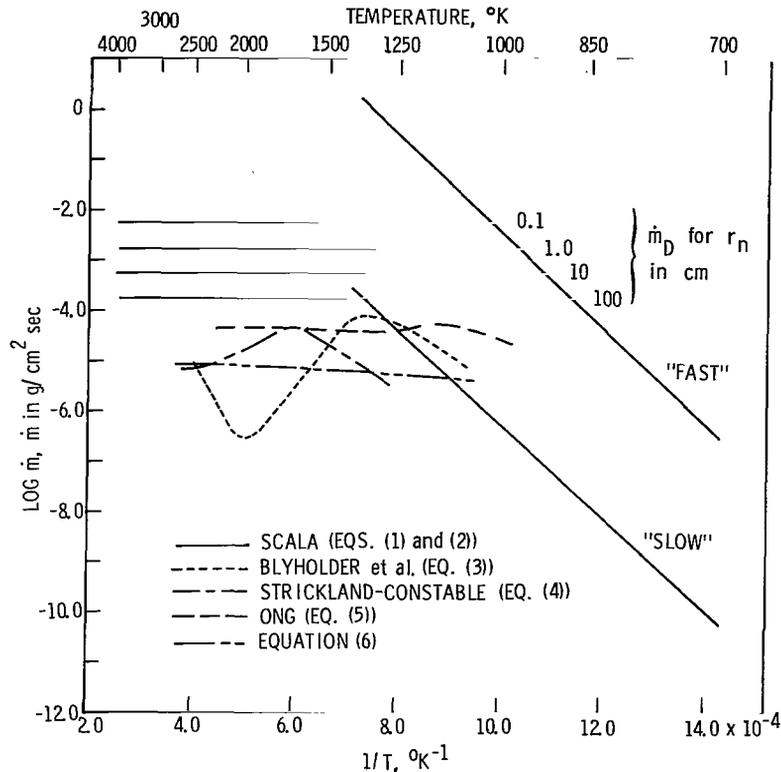


Figure 3.- Comparison of carbon-oxidation-rate expressions at $p_a = 0.01$ atm.

note that the reaction rates predicted by the kinetic expressions in table 1, when compared with Scala's "fast" and "slow" rate bounds, are much closer to the "slow" bound with the one exception of the high rates predicted by the expression of Vulis. [For an explanation of why the rates predicted by Vulis are so high, see footnote (e) of table 1.] It is reassuring, then, that the present high-temperature-rate expressions form a more natural continuation of the "slow" rate bound than they do of the "fast" rate bound.)

At pressures of 0.01 atm, none of the four high-temperature-rate expressions predict a reaction rate fast enough to reach the maximum transport limits, even for a nose radius as large as 100 cm. At the higher pressures of 1 atm and 100 atm, and with the exception of the curve of Blyholder et al.,³ these rate expressions predict reaction rates below 2500° K which equal or exceed the transport limits only for relatively large nose radii. This result clearly indicates that for a wide variety of combinations of pressure, temperature, and nose radii, the maximum attainable rate will be determined by chemical kinetics and not by transport limitations. This statement is not to be interpreted to imply

³The reason the curve of Blyholder et al. (ref. 2) differs so noticeably from the others may be because Blyholder et al. developed their kinetic expression from data obtained at pressures far below the range of pressures in figures 3 to 5.

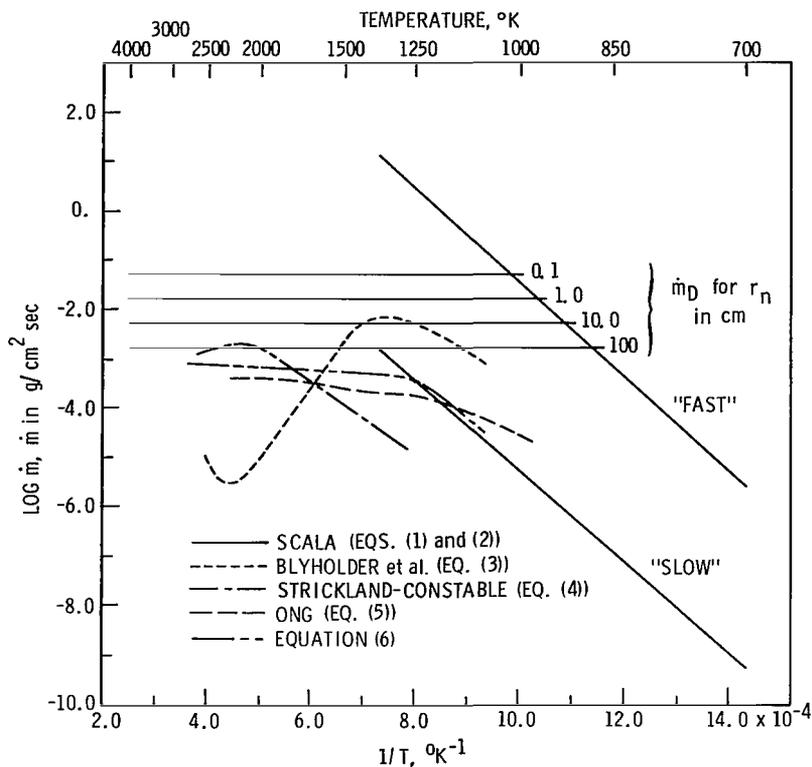


Figure 4.- Comparison of carbon-oxidation-rate expressions at $p_a = 1$ atm.

that the carbon-oxygen reaction at high temperatures is never influenced or limited by oxygen transport. Certainly, at sufficiently low flow rates the reaction may well become limited by transport. But what is indicated is that at high temperatures the kinetics of the reaction are much slower than has generally been suspected on the basis of linear extrapolation of Scala's (ref. 23) "slow" and "fast" rate expressions; therefore, it cannot be assumed that a transport limitation inevitably must be reached. Further, to determine experimentally whether a reaction rate is chemically or transport controlled, the effect of environmental conditions of temperature, pressure, and flow velocity in relation to specimen size (and also carbon type) on the reaction rate must be considered; certainly no definitive statement predicting transport control can be made merely on the basis of the shape of the rate curve as a function of temperature.

The kinetic expression which appears most reliable for estimating the oxidation rate of pyrolytic graphite at high temperatures is that of Strickland-Constable and coworkers (eq. (4)). For estimating the oxidation rates of other less graphitic carbons, the case is not so clear. The kinetic expression of Blyholder et al. (eq. (3)) is not as appropriate for use at normal pressures as the remaining expressions (eqs. (5) and (6)) because it is

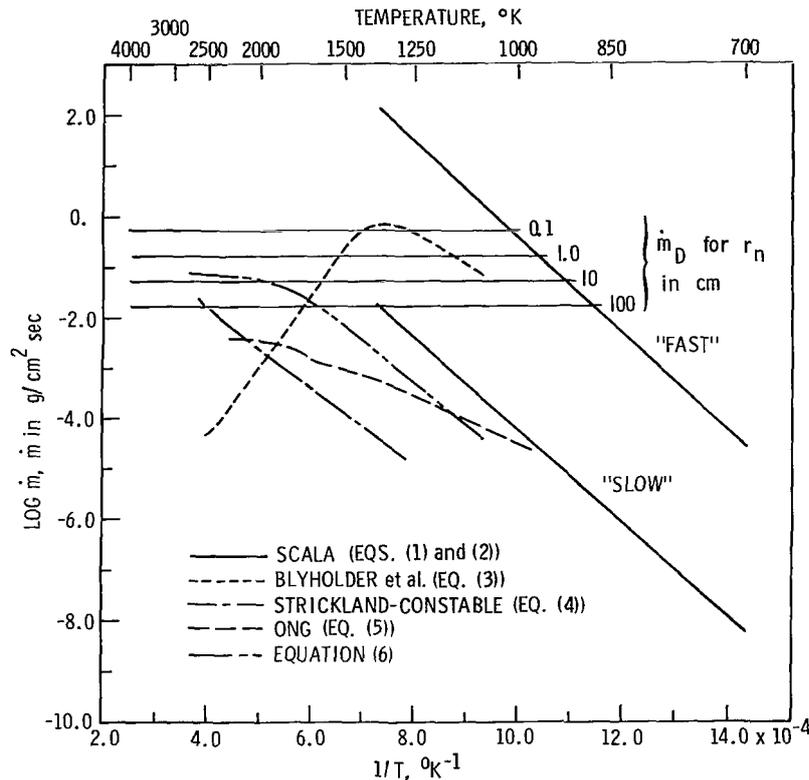


Figure 5.- Comparison of carbon-oxidation-rate expressions at $p_a = 100$ atm.

based on data all obtained at oxygen pressures below 2×10^{-2} torr (some pressures were as low as 5×10^{-5} torr). These data were extrapolated in reference 2 to the common pressure of 10^{-2} torr in order to formulate a kinetic expression. No test of the resulting kinetic expression was made at other pressures. The kinetic expression developed by Ong for artificial graphite (eq. (5)), although particularly appealing because of its strong theoretical foundation, suffers from possible influences of transport interference because of its dependence on the rate data of Okada and Ikegawa for the evaluation of several constants. The kinetic expression given by equation (6), which is based on the data of Golovina and Khaustovich for an electrode carbon, although free of transport interference, suffers from certain theoretical oversimplifications as mentioned earlier. Nevertheless, its use appears preferred because it both fairly adequately describes the data and is simple to use.

CONCLUDING REMARKS

A large body of experimental data exists, convincingly demonstrating that the oxidation rate of carbon passes through a maximum with increasing temperature. Such a

maximum has been observed for such diverse carbons as pyrolytic graphite, artificial graphite, and vitreous carbon. At temperatures above the maximum, a rate decrease followed by a subsequent rate increase has often been observed. Thus, it is clear that the mere existence of a nonlinear rate curve on an Arrhenius plot is insufficient proof of transport influence in a reaction; in order to determine if a reaction is truly kinetically or transport controlled, effects of temperature, pressure, specimen size, flow velocity, and carbon type on the reaction rate must be considered.

Four kinetic expressions based on kinetic data obtained at high temperatures have been presented and compared at air pressures of 0.01 atm, 1 atm, and 100 atm. Above about 1700° K, all these expressions predict mass-loss rates one or more orders of magnitude below that predicted by a linear extrapolation of Scala's "slow" kinetic expression (Tech. Inform. Ser. No. R62SD72). At the pressures of these comparisons, the kinetic expression of Blyholder et al. (J. Phys. Chem., vol. 62, no. 3, 1958) is felt to be of doubtful reliability because it was formulated from data obtained at considerably lower pressures. Comparison of the other three rate predictions with theoretical maximum stagnation-point transport-limited rates of Scala (Tech. Inform. Ser. No. R62SD72) shows that only for relatively large nose radii will transport limitations be encountered below 2500° K; that is, in many practical situations, the maximum attainable rate will be predicted by kinetic considerations. Obviously, however, at sufficiently low flow rates the reaction may well be transport limited.

For estimating the oxidation rate of pyrolytic graphite at high temperatures and normal pressures, the rate expression of Strickland-Constable and coworkers (Carbon, vol. 1, no. 3, 1964; and Second Conference on Industrial Carbon and Graphite, Soc. Chem. Ind. (London), 1966) appears to be preferred:

$$\dot{m} = \frac{12k_A k_B p_{O_2}^2}{(1 + k_z p_{O_2})(k_T + k_B p_{O_2})} + \frac{12k_T k_B p_{O_2}}{k_T + k_B p_{O_2}}$$

where

$$k_A = 20e^{-30\,000/RT}$$

$$k_B = 4.46 \times 10^{-3} e^{-15\,200/RT}$$

$$k_T = 1.51 \times 10^5 e^{-97\,000/RT}$$

$$k_z = 21.3e^{4100/RT}$$

\dot{m} = Mass-loss or reaction rate, g/cm²sec

p_{O_2} = Oxygen pressure, atm

For other less graphitic carbons, the rate expression developed in the present paper based on the data of Golovina and Khaustovich (Eighth Symposium (International) on Combustion, Williams & Wilkins Co., 1962) appears preferred:

$$\dot{m} = \frac{k_1 k_2 p_{O_2}}{k_1 p_{O_2} + k_2}$$

where

$$k_1 = 5.48 \times 10^{-3} e^{-2000/RT}$$

$$k_2 = 5.21 \times 10^3 e^{-40\,000/RT}$$

\dot{m} = Mass-loss or reaction rate, g/cm²sec

p_{O_2} = Oxygen pressure, atm

As a final point, it is recognized that certain contradictory aspects exist in the data discussed, for example, the location of the rate maximum, the magnitude of the reaction rate, and effects of thermal accommodation, and furthermore, that a general uncertainty exists regarding the true kinetic mechanism. Certainly, an understanding of the carbon-oxygen reaction at high (or even low) temperatures is far from complete. Particular areas requiring study include the effects of inert diluents, the determination of pressure dependence over a wide range of pressure (particularly at higher pressures), the role of thermal accommodation and reaction hysteresis, as well as the problem of why the reaction rates of diverse carbons often differ so markedly.

Langley Research Center,

National Aeronautics and Space Administration,

Hampton, Va., May 5, 1971.

APPENDIX A

ADDITIONAL REACTION-RATE DATA AT HIGH TEMPERATURES

In addition to the kinetic expressions and data already discussed, results of a number of other studies of the carbon-oxygen reaction at high temperatures have also been published. (See refs. 15 to 22.) These studies lend further support to the argument that reaction rate, and not oxygen transport, is often the rate-controlling mechanism. Furthermore, a rate maximum was observed in all of these studies. One of the more impressive of these studies is that of Lewis, Floyd, and Cowlard (ref. 15) who approached their study with an expressed concern that perhaps observed rate maxima were not truly associated with the reaction itself but were produced by experimental techniques. Of particular concern to them in this regard was the possible effect of thermal accommodation (i.e., cold gas and hot surface). Results of their experimental study did show that thermal accommodation had an effect on reaction rate (higher gas temperatures resulted in higher reaction rates at the same specimen surface temperature), but the shape of the reaction-rate curve did not change significantly; that is, rate maxima were still observed. Although the study of thermal accommodation effects was conducted on the carbon-carbon dioxide reaction, it may be expected that the carbon-oxygen reaction would behave qualitatively similarly. In the oxidation of vitreous carbon in a 0.1 O₂ and 0.9 argon mixture at 2 atm, a rate maximum occurred at 2050° K and a minimum at 2750° K. Other studies of the oxidation rates of pyrolytic graphite, vitreous carbon, and artificial graphite in CO₂ demonstrated that both the location and the magnitude of the maximum are dependent on carbon type.

Other interesting reaction-rate phenomena have been reported by Rosner and Allendorf (refs. 16 to 20) who studied the reaction of carbon with both molecular and atomic oxygen in the temperature range 1100° K to 2100° K at oxygen pressures of 10⁻² torr. In addition to the low pressure of their tests which minimizes transport influence, transport effects were ruled out on the basis that flow velocity had no effect on reaction rate. (See refs. 17 and 20.) Their results, expressed in terms of oxidation probability,⁴ showed that (1) a rate maximum exists for both pyrolytic and artificial graphite in both molecular and atomic oxygen, (2) atomic oxygen is more effective in removing carbon atoms than is molecular oxygen, (3) artificial graphite is more reactive than the c-face of pyrolytic graphite, and (4) the highest oxidation probability in any of

⁴Defined as the ratio of the number of carbon atoms removed from the surface to the total number of reactant collisions with the surface. In two early papers (refs. 16 and 17), the magnitude of the oxidation-rate probability was erroneously reported too high. This was corrected in subsequent papers. (See refs. 19 and 20.)

APPENDIX A – Concluded

the tests was about one-half. This last point is of particular importance because it says that, even at the high temperatures of the study, a maximum of only one-half as many carbon atoms are being removed from the surface as the number of oxygen atoms striking the surface. When the oxidation probabilities of Rosner and Allendorf (ref. 20) are converted to conventional reaction rates and compared with the reaction-rate data of Blyholder et al. (ref. 2) shown in figure 1, their pyrolytic-graphite data closely follow the data of Sihvonen, and their artificial-graphite data describe a curve similar in shape, but higher than that of Eucken.

A particularly interesting hysteresis effect in the oxidation rate of carbon has been reported by Duval (ref. 21) who reacted graphitic and nongraphitic carbon filaments in oxygen in the pressure range 5×10^{-5} to 3×10^{-3} torr. In addition to the usual rate maxima, he observed that a carbon, having once reached a constant reaction rate at a given temperature, will, when reacted at a new temperature, react at an initial rate which is higher or lower than the final steady-state rate at the new temperature, depending on whether the new temperature is higher or lower than the previous reaction temperature; that is, the initial rate of reaction at a given temperature was found to depend on the conditions of reaction immediately preceding. This result may be of great importance when dealing with rate transients due to changes in surface temperature. Another report of a rate maximum in the oxidation rate of carbon was given by Audubert and Busso (ref. 22) in their study of the reaction rate of electrically heated carbon filaments with air at 20 torr. The rate maximum occurred at about 1825° K.

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