A Semiquantitative Prediction of the Erosion of Graphite Nozzle Inserts

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The erosion of graphite throat inserts is shown to be explicable on the basis of a chemical mechanism if account is taken of the chemical composition of the exhaust stream, the geometrical and temperature history of the insert, the ballistic effects of erosion, the rates of diffusion of the molecular species through the boundary layer, and the chemical kinetics of the surface reactions. Semiquantitative agreement with experiment is demonstrated for a nonaluminized propellant, and the effect of changing temperature and solids loading is predicted correctly. The results show that graphite erosion is kinetically limited by the two processes of diffusion and surface chemical reactions. Pressure is probably the most important single variable involved in erosion, and the relative importance of the two mechanisms is not strongly dependent on pressure or concentration of the corroding species. In general, the amount of erosion which is acceptable seems to be poorly defined. The limiting factor in determining the permissible amount of throat erosion is unlikely to be degradation of specific impulse, chamber pressure, thrust, or mass ratio. More probably, the limit on erosion will be dictated by the practical problem of fabricating inserts which will provide acceptably reproducible erosivities.

Introduction

GRAPHITE is an especially attractive material for use as a rocket nozzle throat insert because of its excellent thermal and physical properties and low density. The principal drawback of graphite is its erosivity. Excessive erosion, particularly nonuniform erosion, is clearly undesirable, though the definition of how much erosion is excessive is usually quite arbitrary.§

There is available a large amount of qualitative data on graphite erosion, but the results are often apparently conflicting, and there is no general agreement concerning the mechanisms involved. Specifically, there is confusion concerning the relative importance of exhaust temperature and chemical composition; also, it is sometimes controversial whether the erosion is attributable to chemical attack or mechanical abrasion by entrained solid particles. It is not surprising that there should be so much uncertainty, because there is a multiplicity of variables involved. Erosivity may conceivably be influenced by the chemical composition, the temperature, and the solids loading of the exhaust stream. Also, the geometry and thermophysical properties of the wall material enter into the problem. Further, pressure is a significant variable, and the pressure change as erosion proceeds is a function of grain design and propellant burning-rate exponent. As would be expected, then, a major source of difficulty in the interpretation of erosion data is the lack of controlled experiments: for example, variation of solids content of the exhaust is generally accomplished by methods that also alter the temperature and chemical composition; also, comparison of reported average rates of erosion may be deceptive because erosion rates may vary greatly during a firing.

An understanding of graphite erosion would obviously be useful for design purposes, and also for directing graphite research concerned with the nozzle insert. The present paper is intended to delineate the relative importance of the factors involved in graphite erosion and to present erosion calculations specifically for rocket nozzle conditions. The treatment will thus differ from others, which have concerned graphite erosion under re-entry conditions (e.g., Refs. 2 and 3), or have been addressed only to a portion of the problem (e.g., Ref. 4).

The erosion process is of such complexity that it does not seem possible to develop a mathematical description that could be termed rigorous. Hence, the usual engineering approach must be used in which an attempt is made to simplify the analysis as much as possible, consistent with the reliability required for the result, with the state of the art, and with the validity of the values employed for the necessary physical properties. The success of such a procedure is usually judged by a comparison of predicted with experimental values, but it should be stated at the start that suitable data are scarce. Although the results look promising on the basis of data for a single system, much more data are needed before a critical appraisal of the analysis can be made.

Summary of Method

A summary of the computational method is given in Fig. 1. For calculational purposes, it was assumed that the rocket would be designed to give a constant chamber pressure in the absence of erosion. All calculations were made by two separate digital computer programs.

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§ An analysis of the ballistic effects of throat erosion is given in Ref. 1, from which most of this paper is taken. The qualitative erosion data and references are also given in Ref. 1.

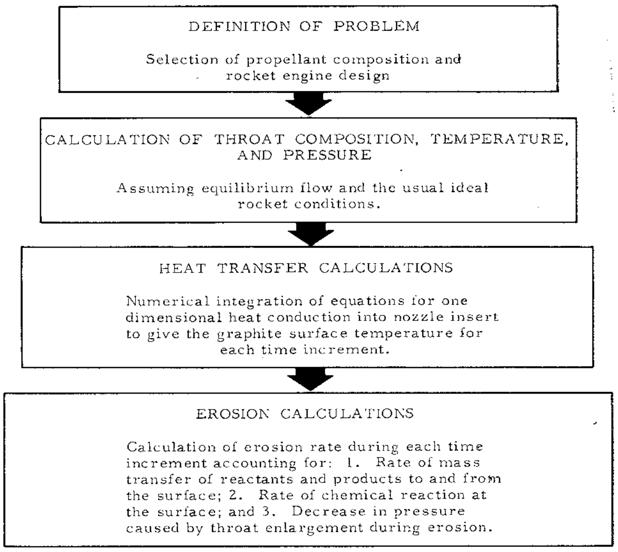
The first program provided the throat composition, temperature, and pressure under the assumptions of equilibrium flow and the usual ideal rocket conditions. We are indebted to the Atlantic Research Corporation for these calculations. It was not convenient to combine this program with the program that solved the heat-transfer and erosion problem. It was therefore assumed that the stream composition at the throat remained constant within a given run. This assumption was shown to be reasonable.

The heat-transfer and erosion calculations, although listed separately in Fig. 1, are performed by the same program, which solves the usual finite difference equations for the unsteady heat-conduction problem, and, for each time increment, also calculates the amount of erosion by chemical reaction.

Solution of the transient heat-conduction problem by means of finite difference equations is well known, and only the specific aspects of the solution used here will be mentioned. Heat convection through the gas film was accounted for as a boundary condition to the conduction equation. The temperature difference driving force was taken as the difference between the surface temperature and the adiabatic wall temperature. The heat-transfer coefficient was calculated from the Bartz equation using transport properties calculated by the equations of Hirschfelder, Curtiss, and Bird as put in graphical form by Brokaw.[5–7] The heat-transfer coefficient was calculated for initial conditions and was continuously adjusted during a run to account for the effects of erosion. Heat transfer to the wall by radiation was neglected. This assumption leads to negligible error except for propellants giving a solid phase at the throat. In the case of aluminized propellants with a graphite insert, the rate of heat transfer to the wall could be as much as 50% low as a result of neglecting radiation, but there are factors that make this uncertain. If one assumes radial symmetry, the equations would properly be written in terms of two distance variables, radial and longitudinal. However, comparison of results for the two-dimensional model with that for a one-dimensional model showed very little difference in surface temperature vs time for a typical nozzle shape and the best estimates of the heat-transfer coefficient in the throat. Thus, longitudinal conduction of heat was neglected. Such an assumption would need re-examination for anisotropic throat materials such as pyrographite. An adiabatic wall was assumed for the boundary condition at the outside surface or rear of the insert, which is a somewhat more severe condition than will actually obtain, but the influence of this boundary condition on the surface temperature is very small for insert thicknesses used. Finally, the thickness of the insert was reduced as indicated by the erosion calculations before starting the next time increment.

Erosion Calculations—Details of Method

The calculations to be described in some detail in this paper are those for the rate of erosion. Under the model used, it is assumed that the mechanism of erosion is chemical reaction between the graphite and some of the species present in the exhaust gas at the throat. The model further assumes that the exhaust gases pass through the throat at $M_a = 1$ at a temperature, pressure, and composition that has been calculated, that a boundary layer of thickness δ is present through which species must diffuse to reach or leave the wall, and that the reaction temperature is the graphite surface temperature calculated as just described. The over-all mechanism is 1) diffusion of the reactants through the boundary layer, 2) chemical reaction at the surface, and 3) diffusion of the products away from the surface. The rate of erosion depends primarily upon the rate of the slowest of these steps.


DEFINITION OF PROBLEM

Selection of propellant composition and rocket engine design

CALCULATION OF THROAT COMPOSITION, TEMPERATURE, AND PRESSURE

Assuming equilibrium flow and the usual ideal rocket conditions.

HEAT TRANSFER CALCULATIONS

Numerical integration of equations for one dimensional heat conduction into nozzle insert to give the graphite surface temperature for each time increment.

EROSION CALCULATIONS

Calculation of erosion rate during each time increment accounting for: 1. Rate of mass transfer of reactants and products to and from the surface; 2. Rate of chemical reaction at the surface; and 3. Decrease in pressure caused by throat enlargement during erosion.

Fig. 1 Summary of computational method.

Implementation of this model requires that the important reactions at the surface and their reaction rates be known and that the boundary-layer thickness and the constituent diffusivities (or the equivalent mass-transfer coefficients) be known. Examination of the species present at the throat for a typical propellant, and consideration of the thermodynamics of the various possible reactions with carbon, led to the conclusion that only the following three reactions need be considered:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \tag{1}$$

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \tag{2}$$

$$2C(s) + H_2(g) \rightarrow C_2H_2(g) \tag{3}$$

Reaction with O_2 was excluded because there is a negligible concentration in the exhaust products over the temperature ranges encountered. Free radical reactions were omitted because of their small concentrations at the surface. For high-temperature propellants, it was assumed that the free radicals H· and OH· would combine during diffusion through the boundary layer, giving H_2 and H_2O.

In developing the equations that follow, the model has been treated as a case of unequal molal counterdiffusion through a stagnant boundary layer. The kinetics of the surface reactions are introduced as boundary conditions. At the start, it should be stated that a more or less rigorous treatment of the diffusion of the species indicated by Eqs. (1–3) coupled with even the simplest reaction rate equations would lead to a set of three coupled differential equations that would have to be integrated simultaneously through the boundary layer. In this initial attack on the erosion problem, the added computational effort for this more exact treatment was not warranted considering the accuracy of some of the data required, such as diffusivities, and considering the scarcity of erosion data with which the calculated erosion can be compared. The simplifying assumptions will be described as they occur in the development. Figure 2 indicates some of the nomenclature. Both reactions in

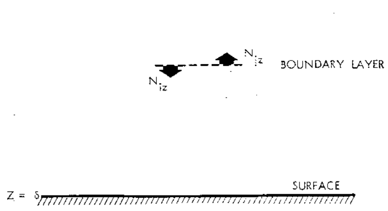


Fig. 2 Boundary-layer model for erosion.

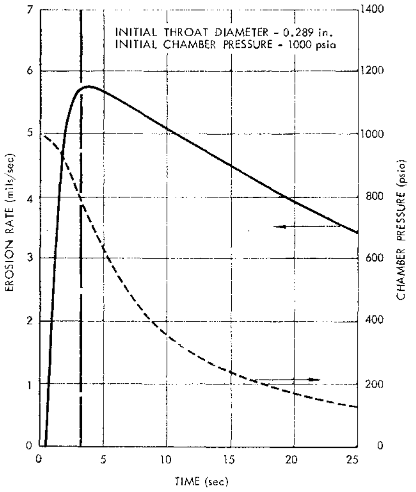


Fig. 3 Calculated erosion rates and chamber pressures for NASA test with Arcite 368—initial time period.

Eqs. (1) and (2) evolve 2 moles of gas for each mole of gas reacting. Thus,

$$N_j = -2N_i \tag{4}$$

where subscripts i and j refer to reactants and products, respectively. For diffusion of one species toward the surface and one product away from the surface, the equation for the flux at a distance z through the boundary layer is[8]

$$N_{iz} = -cD_{ij}(dx_i/dz) + x_i(N_{iz} + N_{jz}) \tag{5}$$

where

c ≡ total molal concentration, moles/ft^3
D_{ij} ≡ diffusion coefficient, ft^2/hr
x_i ≡ mole fraction of component i
N_{iz}, N_{jz} ≡ molal flux of i or j in the z direction, moles/hr-ft^2

When Eq. (5) is extended to a multicomponent diffusion case, the principal change is in the last term on the right, which becomes x_i times the sum of all fluxes present instead of just the sum for a single reaction. Including all the fluxes in Eq. (5) would complicate the integration, and so it was assumed that Eq. (5) could be used in the multicomponent case without changing the last term. This assumption will give erosion rates somewhat higher than would have been obtained with the more correct expressions, but the magnitude of the error is probably small. Also, in extending Eq. (5) to the multicomponent diffusion case, the binary diffusion coefficient D_{ij} was used. This is correct for diffusion of a trace component i in a nearly pure species j, but there would be some error in using this approximation here. Equation (4) may be used to eliminate N_{jz} in Eq. (5), and the resulting equation can be integrated across the boundary layer with the following boundary conditions:

$$\begin{aligned} &\text{at } z = 0 \qquad x_i = x_{i0} \\ &\text{at } z = \delta \qquad x_i = N_{iz}/cK \end{aligned} \tag{6}$$

where

x_{i0} ≡ mole fraction of i in the main stream at the throat
K ≡ first-order rate constant for the reaction of i with carbon at the surface

It might be noted that the last boundary condition is time varying, since K is a function of temperature which is a function of time. The absence of a time derivative in using Eq. (5) implies that the change in inventory of the diffusing species in the boundary layer is neglected compared to the amount of the species that diffuses through the boundary layer. A further assumption can be summarized by the following equation:

$$cD_{ij}/\delta = k_{ia} \tag{7}$$

where k_{ia} is the mass-transfer coefficient for the case of turbulent flow, the subscripts indicating that the diffusivity used in the generalized correlation for k_{ia} is the diffusion of i in air rather than i in j as suggested by the diffusivity D_{ij}. The solution, using Eqs. (4–7), is

$$N_{iz} = k_{ia} \ln[(1 + x_{i0})/(1 + N_i/cK)] \tag{8}$$

Equation (8) was used in the erosion calculations at each time increment for $i = CO_2$ and also $i = H_2O$. The mass-transfer coefficients were calculated from the Gilliland-Sherwood equation[9]

$$k_{ia}D/D_{ia} = 0.023N_{Re}\,0.81N_{Sc}0.44 \tag{9}$$

where

D ≡ throat diameter, ft
D_{ia} ≡ binary diffusion coefficient of i in air, lb-moles/ft-hr
D_v ≡ volumetric diffusivity, ft^2/hr
$\bar{M}$ ≡ average molecular weight
N_{Re} ≡ $DV\rho/\mu$ = Reynolds number
N_{Sc} ≡ $\mu/\rho D_v = \mu/D_{ia}\bar{M}$ = Schmidt number
V ≡ velocity, ft/hr
μ ≡ viscosity, lb/ft-hr
ρ ≡ density, lb/ft^3

Equations such as Eq. (9) are based on the analogy between heat and mass transfer. There is no direct experimental evidence for the validity of this equation at the conditions of flow and temperature in a rocket nozzle, but, even assuming the analogy to be valid, there are corrections to the mass-transfer coefficient from Eq. (9) which could be made to account for the high rates of mass transfer. These effects could be included by methods outlined by Bird, Stewart, and Lightfoot (Ref. 8, p. 656). The final term to be discussed in the use of Eq. (8) is the reaction rate constant K. Rate data are correlated by Khitrin and by Ergun for the reactions of carbon with CO_2 and H_2O.[10, 11] Khitrin interprets the data in terms of the first-order rate equation, whereas Ergun bases the interpretation on the rate determining step of CO(*ads*) → CO(*g*) for both reactions. Neither reports data above 1900°K. For this analysis, the rate constant data from Khitrin were selected because they appeared to be more nearly applicable to the situation of interest and also because they would give the highest erosion rates. In making this choice, we do not suggest that the Khitrin data are more reliable. The Khitrin data are represented by

$$\log K = 8.67 - 9200/T \tag{10}$$

where T is in °K.

As an approximation, the rate constant for the C-CO_2 reaction was assumed to apply to the C-H_2O reaction, although at 1500°K the rate constant for water is 60% higher

Table 1 Characteristics of propellants used in NASA erosion measurements

Component	Arcite 368, mole fraction at throat	Arcite 373, mole fraction at throat
CO_2 (*g*)	0.112	0.005
H_2O (*g*)	0.392	0.050
H_2 (*g*)	0.057	0.435
Al_2O_3 (1)	...	0.086
Stagnation T, °K	2860.0	3324.0
Throat pressure (initial), psia	570.6	576.8
Burning rate exponent	0.44	0.22

than that for CO_2. As a further approximation, the $H\cdot$ and $OH\cdot$ in the freestream were formally added to form H_2O and H_2.

The contribution of the C-H_2 reaction [Eq. (3)] to the erosion mechanism will show little effect below 2500°K, and above that temperature one may assume equilibrium at the surface for all three carbon reactions. Thus, for the C-H_2 reaction, the erosion was determined by the rate of mass transfer of $C_2H_2(g)$ from the surface for which the equation for the flux is

$$N_{C_2H_2} = k_{C_2H_2}x_{C_2H_2} \tag{11}$$

The mole fraction of C_2H_2 at the surface is given by Eq. (11), which is derived by assuming chemical equilibrium at the surface for the three reactions being considered and also considering rates of mass transfer through the boundary layer of all reactants and products:

$$X_{C_2H_2} = \frac{-(k_{H_2O}\bar{x}_{H_2O}/k_{C_2H_2}) + \bar{x}_{H_2}}{(1/K_3) + (k_{C_2H_2}/k_{H_2})} \tag{12}$$

In Eq. (12), the k's were computed from Eq. (9), the bars over the x's indicate bulk stream values, and K_3 is the equilibrium constant for the C-H_2 reaction. Equations (11) and (12) were tested on the recent data of Rogers and Sesonske, giving a calculated erosion rate at initial conditions of 0.260 mils/sec as compared with the average experimental value of 0.164 at 3028°K and 190 psi.[12]

The vaporization of graphite as a mechanism contributing to erosion was examined by a method outlined by Delaney and Eagleton.[13]

The carbon loss at 143 psi, taking into account species C_1, C_2, C_3, C_4, and C_5, was about 0.64×10^{-4} mils/sec at 3000°K and 0.40 mils/sec at 3800°K. It appears unlikely that loss of graphite through vaporization will be serious.

The total rate of carbon loss was calculated from

$$N_C = N_{CO_2} + N_{H_2O} - 2N_{C_2H_2} \tag{13}$$

The forementioned erosion analysis was combined with the computer program for the heat-transfer calculations as described previously. The heat-transfer and mass-transfer coefficients were continuously adjusted to reflect the changing chamber and nozzle conditions. The throat pressure, after a given amount of erosion for a rocket whose grain is designed for a neutral pressure-time curve in the absence of erosion, was calculated from

$$p(A_t)^{1/(1-n)} = p_0(A_{t_0})^{1/(1-n)} = \text{const} \tag{14}$$

where

A_t ≡ throat area
n ≡ burning rate exponent
p ≡ throat pressure
0 ≡ as subscript, values of p and A_t at zero time

After each erosion calculation, a new throat area and pressure were calculated, and these values were used to calculate new mass- and heat-transfer coefficients.

Comparison of Graphite Erosion Predictions with Experiment

The validity of the treatment was tested by comparison with some experimental results reported by NASA-Lewis Laboratories.[14] In these tests, erosion rates were determined quantitatively by means of pressure and throat diameter measurements. At this writing, data are available for two propellants, Arcite 368 and Arcite 373, which are nonaluminized and aluminized composites, respectively. Pertinent characteristics are given in Table 1. The tests were carried out with an ATJ graphite insert, having an initial throat diameter of 0.289 in. and a wall thickness of 0.45 in.

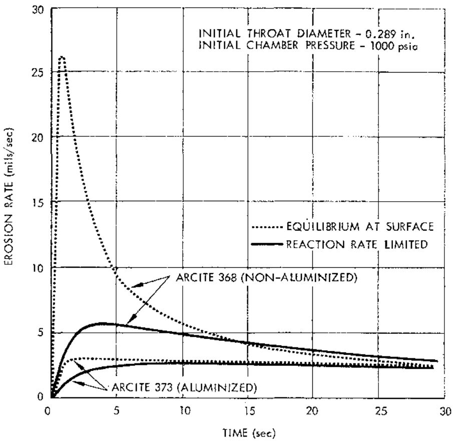


Fig. 4 Calculated erosion rates during NASA tests—effect of assuming infinite reaction rate at surface.

The experiment was carefully designed to give a constant chamber pressure of 1000 psia under conditions of no erosion.

Calculations were carried out as previously described for each propellant and the nozzle dimensions used. The major result was that the calculated average erosion rate during the initial period in which the chamber pressure dropped from 1000 to 800 psia was 4.0 mils/sec for the Arcite 368 (nonaluminized propellant) run. NASA reported a measured 3.4 mils/sec value for the same period. This agreement is considered to be satisfactory within the accuracy of the treatment and the input data. Although quantitative data are not available at this writing, NASA reported that qualitatively the aluminized propellant Arcite 373 was less erosive under the same conditions, which is in accord with the calculations.

Some results of the calculations are given in Figs. 3–6. The following features merit attention:

1) Figure 3 shows that the initially rapid increase in erosion rate is soon arrested by the pressure drop, even though (Fig. 5) the surface temperature continues to rise. This serves to show the considerable importance of pressure in the erosion phenomenon. Because of the dependence of area on the square of the radius, the rate of area change remains about constant during a run, even though the linear erosion rate is decreasing (Fig. 6).

2) Calculations based on chemical equilibrium at the surface (Fig. 4) give an average erosion rate (of the order of 10 mils/sec) for Arcite 368 (nonaluminized) which is much higher than the measured value. This fact serves to indicate that there is indeed a kinetic limitation on graphite erosion.

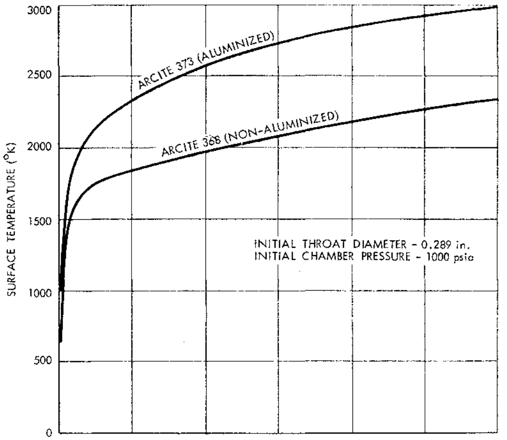


Fig. 5 Calculated surface temperatures during the NASA tests.

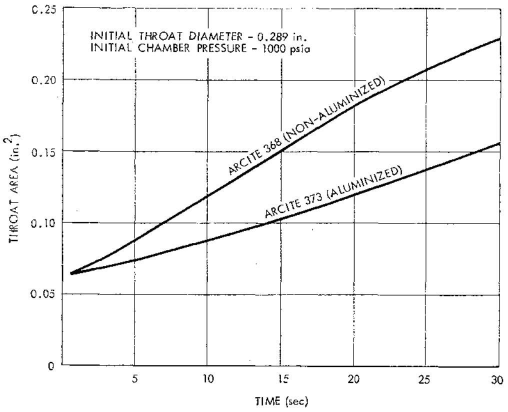


Fig. 6 Calculated throat areas during the NASA tests.

At high temperatures, the erosion becomes entirely mass-transfer limited, and the calculations that include reaction rate data approach those based on equilibrium at the surface.

3) The results give good evidence that the erosion of a graphite insert is predominantly a chemical rather than a mechanical phenomenon. The calculations indicate (Fig. 4) that the nonaluminized system should erode more rapidly than the aluminized propellant, even though the latter is hotter and has a higher particulate loading. This effect is borne out by the NASA experience.

A particularly interesting phenomenon observed in the NASA tests was that after 10 sec of firing, when the throat area had about doubled and the pressure had dropped from 1000 to 470 psia, the test nozzle showed no further erosion for the last 20 sec of the run. The calculations indicate continued erosion. A possible explanation of this phenomenon might be thermal expansion of the insert and permanent set, although more experimental detail would be needed to explain the effect. Tests in which weight as well as dimensional changes were determined would be helpful.

Besides the calculations just described and represented in Figs. 3–6, an additional set of calculations was made to show the relative effects of the two major variables, throat pressure and graphite surface temperature, and also the relative importance of the chemical reaction step as compared with the mass-transfer step. The exhaust gas was assumed to be the same as that for Arcite 368, but in computing the erosion rate and the relative importance of the reaction step, only reaction of the water vapor, the major reacting species, was considered. The erosion rate was calculated for two different pressures (570.6 and 285.3 psia) at various temperatures from 1500°K using Eq. (8). The calculation was also made for Arcite 373 at a pressure of 576.8 psia. The results are shown in Fig. 7. It can be seen that, below 1500°K, very little erosion takes place, and, for a particular propellant, the erosion rate increases almost directly with pressure at all temperatures.

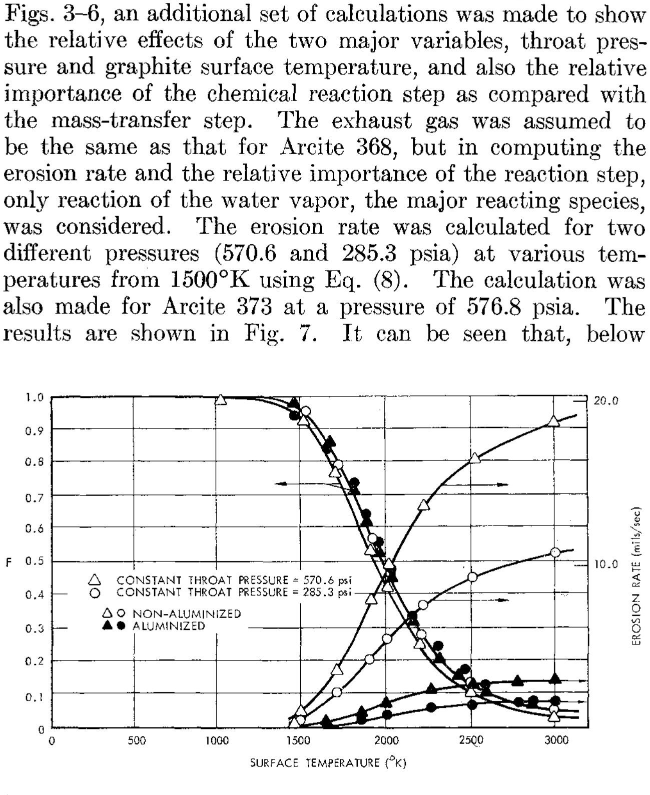


Fig. 7 Fractional improtance of chemical reaction rate step F and erosion rate as a function of temperature and pressure.

The importance of the reaction rate to the erosion rate as a function of surface temperature is also shown in Fig. 7. These curves were constructed by defining a fractional importance of the reaction step F as the fractional differential change in the flux dN_{iz}/N_{iz} divided by the fractional change in the first-order rate constant, dK/K. From Eq. (8) the following equation is obtained:

$$F = \frac{KdN_{iz}}{N_{iz}dK} = \frac{1}{(cK/k_{ia}) + (N_{iz}/k_{ia}) + 1} \tag{15}$$

The use of Eq. (8) rather than Eq. (13) restricts Eq. (15) to a single reaction (that for H_2O) rather than to the over-all process involving all three reactions. However, the differences would be small since the same K was used for both Eqs. (1) and (2) and Eq. (3) is not very important below 2500°K. When $F = 1.0$, it is proper to conclude that the erosion is controlled by the chemical reaction step, whereas if $F = 0$, the reaction rate is of no importance and mass transfer is controlling. Figure 7 shows the two mechanisms to be equally important at about 2000°K, and above this temperature, errors in the reaction rate constant would be more or less unimportant. Calculations similar to those illustrated in Fig. 7 showed that decreasing the rate constant by a factor of two decreased the calculated erosion rate due to that particular reaction by about 33% at 2000°K and only 2.2% at 3000°K. Figure 7 also shows that the relative importance of the reaction rate step is not strongly dependent on throat pressure for the reason that both the reaction rate and the mass-transfer rate increase almost linearly with pressure. The fractional importance of the reaction step is also shown to be relatively independent of the concentration of the corroding species, since the curves for Arcite 368 and Arcite 373 practically coincide, although the concentration of H_2O in the two propellants differs by a factor of 8.

It has been shown that the calculations described in this paper give good agreement with experiment on the basis of only one run and some qualitative observations. It is certainly essential that comparison with other data be made before any conclusion regarding the reliability of the method can be established. Some of the numerous assumptions have been shown or could easily be shown to contribute negligible error to the over-all results. For example, one of the greatest uncertainties is in the chemical reaction rate constants. Not only were the data extrapolated much farther in temperature than would normally be considered safe, but the basis for the extrapolation, the first-order rate assumption, may be invalid. However, it was shown that errors in the rate data are unlikely to contribute significantly to an error in the average erosion rate unless only the initial low-temperature period is considered. On the other hand, if the reaction rate above 2000°K is an order of magnitude lower than predicted from the Khitrin correlation, the importance of the rate step would be much greater than shown in Fig. 7 and better rate data would be desirable. Our results are sensitive to errors introduced in accounting for the mass-transfer phenomena, and uncertainties in this area are likely to remain for some time. Nevertheless, the importance of some of the assumptions could be evaluated at the present time. Comparison with data will still remain the valid test of the method.

References

[1] Jones, W. H. and Delaney, L. J., "An analysis of the materials problem for throat inserts of high energy solid propellant rockets," Institute for Defense Analyses, TR 62-19, UBG 62-559 (October 1962).

[2] Moore, J. A. and Zlotnick, M., "Combustion of carbon in air stream," ARS J. **31**, 1388–1397 (1961).

[3] Nolan, E. J. and Scala, S. M., "Aerothermodynamic be-

havior of pyrolytic graphite during sustained hypersonic flight," ARS J. **32**, 26–35 (1962).

[4] Bro, P. and Steinberg, S., "Study of chemical surface reactions in a high temperature flow system with arc heated gases," ARS J. **32**, 528–532 (1962).

[5] Bartz, D. R., "A simple equation for rapid estimation of rocket nozzle heat transfer coefficients," Jet Propulsion **27**, 49–51 (1957).

[6] Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., *The Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Chap. 7.

[7] Brokaw, R. S., "Alignment charts for transport properties, viscosity, thermal conductivity and diffusion coefficients for non-polar gases and gas mixtures at low density," NASA TR-R81 (1961).

[8] Bird, R. B., Stewart, W. E., and Lightfoot, E. N., *Transport Phenomena* (John Wiley and Sons, Inc., New York, 1960), p. 571.

[9] McCabe, W. L. and Smith, J. C., *Unit Operations of Chemical Engineering* (McGraw-Hill Book Co., Inc., New York, 1956), p. 623.

[10] Khitrin, L. N., "Fundamental principles of carbon combustion and factors intensifying the burning of solid fuels," *Proceedings of the Sixth (International) Symposium on Combustion* (1956).

[11] Ergun, S., "Kinetics of the reactions of carbon dioxide and steam with coke," U. S. Bureau of Mines, Bull. 598 (1962).

[12] Rogers, J. D. and Sesonske, A., "Graphite-hydrogen-methane kinetics above 1600°K," Los Alamos Scientific Lab., N-1-590 (1962).

[13] Delaney, L. J. and Eagleton, L. C., "A test of the assumption of interfacial equilibrium in measurements of the gas film mass transfer coefficient," Am. Inst. Chem. Engrs. J. **8**, 418–420 (1962).

[14] Signorelli, J. R. A., Frecke, T., and Johnston, J. R., NASA, Cleveland, Ohio (1962); unpublished data.