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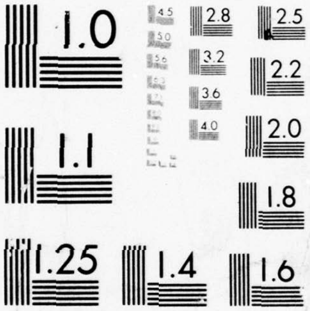

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Analytic Solutions for Carbon Sublimation in Atmospheres of Elemental Carbon, Hydrogen, Nitrogen, and Oxygen

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Final Report

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This report has been reviewed by the Office of Information (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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Analytic solutions have been obtained for the equilibrium sublimation of a carbon surface in atmospheres whose elemental composition consists of carbon, hydrogen, oxygen, nitrogen, and an inert element. The solutions are expressed in simple algebraic expressions for the surface mass transfer parameter (B') and are computationally trivial, requiring only the evaluation of a quadratic equation. The analytic expressions are essentially exact and

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include an arbitrary number of carbon sublimation species and all the dominant gas phase reactions, while ignoring only those species which exist in trace amounts. The solutions are in excellent agreement with exact results from the ACE chemistry code.

With the exception of the expressions for simple binary systems (one sublimation species and no gas phase reactions), the present results are the only known analytic solutions for B'. The results are extremely general and are applicable to carbon sublimation in a wide variety of planetary atmospheres (including air) and ablation test facilities (arc jets, rocket engines, and ballistic ranges). The solutions should be particularly suited for applications in which the atmospheric elemental composition is changed frequently and in situations where a knowledge of the analytic behavior of B' with temperature is desired.

PREFACE

The author would like to express his appreciation to Dr. Howard J. Deacon, Jr., who generated the ACE solutions used in this report and contributed a number of helpful suggestions during this effort.

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INTRODUCTION

The sublimation of carbon may be divided into several regimes depending upon whether the solid-vapor and gas phase reactions are in equilibrium. Nonequilibrium effects for both the gas phase reactions and the solid vaporization reaction are significant only at low pressures. Since the intended application of this work is for high pressure planetary entry calculations, only the equilibrium case is considered. That is, all gas phase reactions are presumed to be in equilibrium, and the solid carbon surface is assumed to be in equilibrium with each of the carbon sublimation species.

The equilibrium sublimation of carbon has been extensively investigated in the literature for various assumptions concerning the sublimation species and the dominant gas phase reactions. In particular, the use of differing vapor pressure laws (for the sublimation species) and associated thermochemical data (heats of formation and free energy functions for each species) leads to a considerable variation in predicted surface mass transfer coefficients (B'). The Bibliography is by no means complete but is typical of the available work.

The one common feature of the referenced work (with the exception of Ref. 1) is that the surface mass transfer coefficients were obtained by an iterative numerical scheme as is usually employed in general purpose equilibrium chemistry codes such as ACE (Ref. 2). Bartlett (Ref. 1), by

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[1] Bartlett, E. P., "Analytical and Graphical Prediction of Graphite Ablation Rates and Surface Temperatures During Reentry at 25,000 to 45,000 Feet per Second," Air Force Flight Test Center, Edwards Air Force Base, California, TDR-63-40, March 1964.

[2] Powars, C. A., and R. M. Kendall, "User's Manual--Aerotherm Chemical Equilibrium (ACE) Computer Program," Aerotherm Corporation, May 1969.

assuming only one sublimation species (C_3) and ignoring carbon-nitrogen reactions, obtained an explicit, analytic solution for the surface mass transfer coefficient. For carbon sublimation in an atmosphere of elemental carbon, nitrogen, oxygen, and an inert (denoted by I) monatomic species, it is possible to generalize Bartlett's work to include any number of carbon sublimation species and all of the significant carbon-nitrogen reactions, while still obtaining an analytic solution for the mass transfer parameter (B'). Similarly, an analytic solution is possible in an atmosphere of C, N, O, H and I.

Apparently, it is not generally (if at all) recognized that analytic solutions are possible for the equilibrium sublimation of carbon in many atmospheres of interest. It is the purpose of this report to present these solutions for the surface mass transfer coefficient and compare them with exact results obtained from the ACE computer code.

Aside from their own intrinsic elegance, there exist several utilitarian reasons for developing analytic solutions for B'. First, precomputed values of B' are valid only for a specified set of species thermochemical data and for an atmosphere of fixed elemental composition. If the thermochemical data or the atmospheric composition is changed, the value of B' must be recalculated. Analytic solutions eliminate the need to precompute B', thereby allowing the rapid assessment of differing thermochemical data and atmospheric composition upon the mass transfer. Secondly, the solution of the energy equation coupled to the surface energy balance involves an iterative scheme which is quite sensitive to the temperature derivative of B'. This derivative is difficult to evaluate accurately from tabulated values of B', but is easily calculated from an analytic solution.

The analytic solution for carbon sublimation in an atmosphere of elemental carbon, nitrogen, oxygen, and an inert species is essentially exact and is presented in Section II. The inclusion of hydrogen into the atmospheric composition is treated in Section III and yields an analytic solution which is slightly less precise than that of Section II (due to the neglect of carbon-nitrogen reactions), but which is still in excellent agreement with exact solutions.

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SECTION II

CARBON SUBLIMATION IN A C-N-O-I ATMOSPHERE

As discussed earlier, the objective is to obtain an analytic expression for the surface mass transfer parameter (B'). The elemental composition of the atmosphere is assumed to consist of carbon, nitrogen, oxygen, and an inert monatomic species (denoted by I). This specification includes a variety of atmospheres of interest, such as air and a Mars atmosphere consisting of N_2, CO_2 and Ar.

The independent variables are the surface temperature and pressure and the elemental composition at the boundary layer edge. By definition, the elemental mass fractions (denoted by a superscript tilde) must sum to unity.

$$\tilde{K}_{C_e} + \tilde{K}_{O_e} + \tilde{K}_{N_e} + \tilde{K}_{I_e} = 1 \qquad (1)$$

where the subscript e refers to boundary layer edge conditions.

Since the solid carbon surface is assumed to be in equilibrium with its vapor, the partial pressure of each sublimation species is equal to its vapor pressure. The vapor pressures, presented in Appendix A, are known functions of surface temperature. It is precisely this knowledge of the partial pressures of the carbon species which allows an analytic solution. Thus, in all that follows, the partial pressures of the carbon species have been replaced by their respective vapor pressures.

A number of commonly employed assumptions are used to simplify the problem. All the oxygen at the carbon surface is assumed to be bound up in CO and thus is not available for the formation of CO_2, O_2, NO, etc. The surface temperature is presumed to be low enough so that monatomic oxygen and nitrogen are not present at the wall. Ionized species are ignored.

An arbitrary number of carbon sublimation species are allowed in the formulation and all of the dominant carbon-nitrogen reactions are included. The carbon-nitrogen reactions may be expressed in any form as long as the system is linearly independent. Furthermore, since all the carbon sublimation species are in equilibrium with one another, the carbon-nitrogen reactions may be expressed in terms of any one (or combination) of the sublimation species. With these points in mind, the carbon-nitrogen reactions are expressed as

$$
\begin{aligned}
&N_2 + 2C \rightarrow 2\,CN \\
&C_2N_2 \rightarrow 2\,CN \\
&C_4N_2 \rightarrow 2\,CN + 2C \\
&C_2N \rightarrow CN + C
\end{aligned}
\qquad (2)
$$

Notice that no dissociation reactions involving the carbon sublimation species are explicitly included in the formulation. This is not necessary because the use of the carbon vapor pressure laws guarantees gas phase equilibrium among the sublimation species.

The elemental mass balances at the wall are given by

$$
\begin{aligned}
\tilde{K}_{O_w} &= \frac{16}{28} K_{CO} \\
\tilde{K}_{N_w} &= K_{N_2} + \frac{14}{26} K_{CN} + \frac{28}{52} K_{C_2N_2} + \frac{28}{76} K_{C_4N_2} + \frac{14}{38} K_{C_2N} \\
\tilde{K}_{C_w} &= \frac{12}{28} K_{CO} + \frac{12}{26} K_{CN} + \frac{24}{52} K_{C_2N_2} + \frac{48}{76} K_{C_4N_2} + \\
&\quad + \frac{24}{38} K_{C_2N} + \sum K_{C_i} \\
\tilde{K}_{I_w} &= K_I
\end{aligned}
\qquad (3)
$$

where subscript w refers to conditions at the wall. The molecular weight is given by

$$\frac{1}{M} = \frac{K_{CO}}{28} + \frac{K_{N_2}}{28} + \frac{K_{CN}}{26} + \frac{K_{C_2N_2}}{52} + \frac{K_{C_4N_2}}{76} + \frac{K_{C_2N}}{38} + \frac{K_I}{M_I} + \sum \frac{K_{C_i}}{M_{C_i}} \tag{4}$$

Note that the inert species is characterized solely by its molecular weight (M_I).

The equilibrium relationships for the carbon-nitrogen reactions may be expressed in terms of the partial pressures of the products and reactants. This yields

$$\begin{aligned} P_{N_2} &= \alpha_1 P_{CN}^2 \\ P_{C_2N_2} &= \alpha_2 P_{CN}^2 \\ P_{C_4N_2} &= \alpha_3 P_{CN}^2 \\ P_{C_2N} &= \alpha_4 P_{CN} \end{aligned} \tag{5}$$

The α coefficients are defined in terms of the pressure equilibrium constants for the reactions (presented in Appendix B) and the vapor pressure of monatomic carbon. Therefore, the α coefficients are known functions of the surface temperature.

$$\alpha_1 \equiv \frac{1}{P_C^2 K_{p_1}} \qquad \alpha_2 \equiv \frac{1}{K_{p_2}}$$

$$\alpha_3 \equiv \frac{P_C^2}{K_{p_3}} \qquad \alpha_4 \equiv \frac{P_C}{K_{p_4}} \tag{6}$$

The elemental mass fractions at the wall are related to their boundary layer edge values and the surface mass transfer coefficient by the analogy between mass and heat transfer (assuming equal diffusion coefficients and Lewis and Prandtl numbers of unity). This yields

$$\tilde{K}_{O_w} = \frac{\tilde{K}_{O_e}}{1 + B'}$$

$$\tilde{K}_{N_w} = \frac{\tilde{K}_{N_e}}{1 + B'}$$

$$\tilde{K}_{I_w} = \frac{\tilde{K}_{I_e}}{1 + B'}$$

$$\tilde{K}_{C_w} = \frac{B' + \tilde{K}_{C_e}}{1 + B'}$$

$$B' \equiv \frac{\dot{m}}{\rho_e u_e C_H} \qquad (7)$$

The partial pressure of any constituent is given as

$$P_i = \frac{PMK_i}{M_i} \qquad (8)$$

The set of Eqs. (3) may be expressed in terms of partial pressures by multiplying through by the product of pressure and molecular weight. After this multiplication, the equations are combined with Eqs. (4), (5), and (7) to yield a quadratic for the partial pressure of CN. The algebraic details are presented in Appendix C.

$$(1+28\lambda)(\alpha_1+\alpha_2+\alpha_3)\,P_{CN}^2 + (1+14\lambda)(1+\alpha_4)\,P_{CN} + \\ - \left(P - \sum P_{C_i}\right) = 0$$

$$\lambda \equiv \frac{\tilde{K}_{O_e}}{16\,\tilde{K}_{N_e}} + \frac{\tilde{K}_{I_e}}{M_I\tilde{K}_{N_e}} \qquad (9)$$

After the quadratic is solved for P_{CN} (use plus sign in front of radical for the correct root), the remaining partial pressures are calculated from Eq. (5). The mass transfer parameter is obtained from the elemental carbon mass balance of Eq. (3) and is obtained as (see Appendix C)

$$B' = B^* - \tilde{K}_{C_e} + \frac{\tilde{K}_{N_e}\left[(12+24\alpha_4)P_{CN} + (24\alpha_2+48\alpha_3)P_{CN}^2 + \sum M_{C_i}P_{C_i}\right]}{14(1+\alpha_4)P_{CN} + 28(\alpha_1+\alpha_2+\alpha_3)P_{CN}^2}$$

$$B^* \equiv \frac{12}{16}\,\tilde{K}_{O_e} \qquad (10)$$

If it is desired to examine the relative contribution of the carbon-nitrogen species, the appropriate α coefficients of Eq. (5) may be zeroed. If all carbon-nitrogen reactions are deleted, the system of equations is solved for the N_2 partial pressure

$$P_{N_2} = \frac{P - \sum P_{C_i}}{1+28\lambda} \qquad (11)$$

Thus, for no carbon-nitrogen reactions, the mass transfer parameter is

$$B' = B^* - K_{C_e} + \frac{\tilde{K}_{N_e}(1+28\lambda)\sum M_{C_i} P_{C_i}}{28\left(P - \sum P_{C_i}\right)} \tag{12}$$

Note that Eq. (12) is the analog of Bartlett's C_3 only model for an arbitrary number of sublimation species.

If there is no nitrogen in the atmosphere $\left(\tilde{K}_{N_e} = 0\right)$, Eq. (12) yields

$$B' = B^* - \tilde{K}_{C_e} + \left(\frac{B^*}{12} + \frac{\tilde{K}_{I_e}}{M_I}\right)\frac{\sum M_{C_i} P_{C_i}}{P - \sum P_{C_i}} \tag{13}$$

After B' is solved for, the molecular weight at the wall is calculated from the carbon mass balance of Eq. (3).

$$\frac{PM}{1+B'}\left(B' - B^* + \tilde{K}_{C_e}\right) = 12(1+2\alpha_4)P_{CN} + 24(\alpha_2 + 2\alpha_3)P_{CN}^2 + \sum M_{C_i} P_{C_i} \tag{14}$$

After the molecular weight from Eq. (14) is obtained, the species mass fractions may be calculated from the relationship between partial pressure and mass fraction [Eq. (8)].

A closing comment is in order. Notice that the solution could be generalized by including the reduction of CO_2 to CO. This would allow the calculation of diffusion controlled recession at low temperatures. However, at low temperatures, the recession is likely to be rate limited, and the diffusion controlled calculated would provide only an upper bound for the actual mass loss. Furthermore, the inclusion of the CO_2 reduction reaction would yield a quartic to be solved for either the CN or CO partial pressure. Although an analytic solution for a quartic is available, it is considerably more complex than evaluating a quadratic. For these reasons, the CO_2 reaction was not included.

As mentioned earlier, the results of this section may be used for carbon sublimation in air. For Argon free air, the following values are used:

$$\tilde{K}_{O_e} = 0.232$$

$$\tilde{K}_{N_e} = 0.768$$

$$\tilde{K}_{C_e} = 0$$

$$\tilde{K}_{I_e} = 0$$

$$B^* = 0.174$$

$$\lambda = 0.01888 \qquad (15)$$

SECTION III

CARBON SUBLIMATION IN A C-H-O-N-I ATMOSPHERE

In this section, the sublimation of carbon is examined in an atmosphere whose elemental composition consists of carbon, hydrogen, oxygen, nitrogen and an inert monatomic species. The applications of interest for this atmosphere consist of planetary entry cases (e.g., Jupiter) and ablation testing in rocket engines. Since the planetary entry application involves much higher surface temperatures than the rocket engine environment, the analysis is divided into high and low temperature domains.

The inclusion of hydrogen in the elemental composition is accommodated in the formulation by ignoring the carbon-nitrogen reactions. That is, since carbon reacts preferentially with hydrogen, the carbon-nitrogen reactions are assumed to exert only a second-order influence on the surface mass transfer coefficient.

The surface temperature and pressure and the boundary layer edge elemental composition are presumed known. As before, the partial pressures of the carbon sublimation species are equated to their corresponding vapor pressures and are then known functions of temperature. Again, the elemental mass fractions at the boundary layer edge must sum to unity

$$\tilde{K}_{C_e} + \tilde{K}_{H_e} + \tilde{K}_{N_e} + \tilde{K}_{O_e} + \tilde{K}_{I_e} = 1 \qquad (16)$$

The high and low temperature regimes are considered below.

A. HIGH TEMPERATURE REGIME

The surface temperature is presumed to be high enough so that all oxygen is bound in CO. Therefore, CO_2 and H_2O exist only in trace amounts and are ignored. Although the surface temperature is such as to preclude the formation of water vapor, it is assumed to be insufficient to dissociate N_2 or

CO. Thus, monatomic nitrogen and oxygen are not present at the wall. The hydrogen dissociation reaction is included, along with the two dominant carbon-hydrogen reactions and an arbitrary number of carbon sublimation species.

The gas phase reactions are specified as

$$\begin{gathered} C_2H \rightarrow H + 2C \\ C_2H_2 \rightarrow 2H + 2C \\ H_2 \rightarrow 2H \end{gathered} \tag{17}$$

The elemental mass balances and molecular weight at the wall are given by

$$\begin{aligned}
\tilde{K}_{N_w} &= K_{N_2} \\
\tilde{K}_{O_w} &= \frac{16}{28} K_{CO} \\
\tilde{K}_{H_w} &= K_H + K_{H_2} + \frac{2}{26} K_{C_2H_2} + \frac{1}{25} K_{C_2H} \\
\tilde{K}_{C_w} &= \frac{12}{28} K_{CO} + \frac{24}{26} K_{C_2H_2} + \frac{24}{25} K_{C_2H} + \sum K_{C_i} \\
\tilde{K}_{I_w} &= K_I \\
\frac{1}{M} &= \frac{K_{CO}}{28} + \frac{K_{N_2}}{28} + \frac{K_{H_2}}{2} + K_H + \frac{K_{C_2H_2}}{26} + \frac{K_{C_2H}}{25} + \frac{K_I}{M_I} + \sum \frac{K_{C_i}}{M_{C_i}}
\end{aligned} \tag{18}$$

The relationship between the wall elemental mass fractions and the boundary layer edge values is supplied by Eq. (7), with the exception of hydrogen, which is given as

$$\tilde{K}_{H_w} = \frac{\tilde{K}_{H_e}}{1 + B'} \tag{19}$$

The partial pressures for the reactants and products of Eq. (16) are given by

$$P_{C_2H} = \alpha_5 P_H$$

$$P_{C_2H_2} = \alpha_6 P_H^2$$

$$P_{H_2} = \alpha_7 P_H^2 \tag{20}$$

The α coefficients are defined in terms of the equilibrium constants and the vapor pressure for monatomic carbon.

$$\alpha_5 \equiv \frac{P_C^2}{K_{P_5}} \qquad \alpha_6 \equiv \frac{P_C^2}{K_{P_6}}$$

$$\alpha_7 \equiv \frac{1}{K_{P_7}} \tag{21}$$

Equations (18) are multiplied by the product of pressure and molecular weight to cast them in terms of partial pressures. Then, combining Eqs. (7), (18), (19), and (20) yields a quadratic for the partial pressure P_H. The algebraic operations are similar to those of Appendix C.

$$\beta_2(\alpha_6 + \alpha_7)P_H^2 + \beta_1(1 + \alpha_5)P_H - \left(P - \sum P_{C_i}\right)\tilde{K}_{H_e} = 0$$

$$\beta \equiv \frac{\tilde{K}_{N_e}}{28} + \frac{\tilde{K}_{O_e}}{16} + \frac{\tilde{K}_{I_e}}{M_I}$$

$$\beta_1 \equiv \beta + \tilde{K}_{H_e}$$

$$\beta_2 \equiv 2\beta + \tilde{K}_{H_e} \tag{22}$$

After solving the quadratic for P_H, all the remaining partial pressures are easily evaluated. The surface mass transfer parameter is evaluated from the carbon mass balance of Eq. (18) and yields

$$B' = B^* - \tilde{K}_{C_e} + \frac{\beta\left[24\alpha_6 P_H^2 + 24\alpha_5 P_H + \sum M_{C_i} P_{C_i}\right]}{P - \sum P_{C_i} - (\alpha_6 + \alpha_7)P_H^2 - (1+\alpha_5)P_H} \qquad (23)$$

As mentioned earlier, the validity of this expression for B' presumes that the carbon-nitrogen reactions [which were ignored in obtaining Eq. (23)] are insignificant in comparison with the carbon-hydrogen reactions. In the limit that the elemental mass fraction of hydrogen $\left(\tilde{K}_{H_e}\right)$ vanishes, this assumption will become progressively worse. However, if only trace amounts of hydrogen were present, it could be ignored and the mass transfer coefficient evaluated from the results of Section II.

In any event, notice that the carbon-nitrogen reactions were deleted for simplicity and not from necessity. That is, it is possible to include all the carbon-nitrogen reactions of Eq. (2) along with the carbon-hydrogen reactions of Eq. (17) and still obtain an analytic solution for the mass transfer coefficient. However, the determination of the constituent partial pressures would require the solution of a quartic. Although a quartic does possess an analytic solution, it was felt that the additional complexity was not warranted for the intended application.

The molecular weight is obtained from either the hydrogen or carbon mass balances [Eq. (18)]. The hydrogen mass balance yields

$$\frac{PM}{1 + B'} \tilde{K}_{H_e} = (1 + \alpha_5)P_H + 2(\alpha_6 + \alpha_7)P_H^2 \qquad (24)$$

B. LOW TEMPERATURE REGIME

In the previous subsection, the surface temperature was assumed to be high enough so that the water gas reaction was insignificant. At lower temperatures, however, the formation of water vapor and carbon dioxide has a first-order effect on the surface mass transfer. Since this regime may be important for ablation testing in rocket engines, it is considered here.

The surface temperature is assumed low enough so that atomic oxygen, hydrogen, and nitrogen are not present at the wall. All the oxygen is assumed to be bound up in H_2O, CO_2 and CO. Again, an arbitrary number of carbon sublimation species are included, as well as a single carbon-hydrogen reaction. The reactions are

$$H_2O + CO \rightarrow CO_2 + H_2$$

$$C + CO_2 \rightarrow 2\,CO$$

$$C_2H_2 \rightarrow H_2 + 2C \qquad (25)$$

The equilibrium relationships relate the partial pressures of products and reactants.

$$P_{H_2O} = \alpha_8 P_{CO} P_{H_2}$$

$$P_{CO_2} = \alpha_9 P_{CO}^2$$

$$P_{C_2H_2} = \alpha_{10} P_{H_2} \qquad (26)$$

The α coefficients are given by

$$\alpha_8 \equiv \frac{1}{K_{P_8} K_{P_9} P_C} \qquad \alpha_9 \equiv \frac{1}{K_{P_9} P_C}$$

$$\alpha_{10} \equiv \frac{P_C^2}{K_{P_{10}}} \tag{27}$$

The mass balances and molecular weight are given by

$$\tilde{K}_{N_w} = K_{N_2}$$

$$\tilde{K}_{O_w} = \frac{16}{28} K_{CO} + \frac{32}{44} K_{CO_2} + \frac{16}{18} K_{H_2O}$$

$$\tilde{K}_{I_w} = K_I$$

$$\tilde{K}_{H_w} = K_{H_2} + \frac{2}{18} K_{H_2O} + \frac{2}{26} K_{C_2H_2}$$

$$\tilde{K}_{C_w} = \frac{12}{28} K_{CO} + \frac{12}{44} K_{CO_2} + \frac{24}{26} K_{C_2H_2} + \sum K_{C_i}$$

$$\frac{1}{M} = \frac{K_{CO}}{28} + \frac{K_{N_2}}{28} + \frac{K_{CO_2}}{44} + \frac{K_{H_2O}}{18} + \frac{K_{H_2}}{2} + \frac{K_I}{M_I} + \frac{K_{C_2H_2}}{26} + \sum \frac{K_{C_i}}{M_{C_i}} \tag{28}$$

Equations (7) and (19) relate the elemental mass fractions at the wall and boundary layer edge.

If Eqs. (28) are cast into partial pressures, the system may be rearranged to yield a cubic for the partial pressure of CO.

$$AP_{CO}^3 + BP_{CO}^2 + CP_{CO} + D = 0$$

$$A \equiv \alpha_8\alpha_9\left(56\widetilde{K}_{H_e} + 7\widetilde{K}_{O_e} + 8\lambda\right)$$

$$B \equiv \alpha_8\left(7\widetilde{K}_{O_e} + 4\lambda\right) + \alpha_9(1+\alpha_{10})\left(112\widetilde{K}_{H_e} + 7\widetilde{K}_{O_e} + 8\lambda\right)$$

$$C \equiv (1+\alpha_{10})\left(56\widetilde{K}_{H_e} + 7\widetilde{K}_{O_e} + 4\lambda\right) +$$

$$+ 7\,\alpha_8\left(8\widetilde{K}_{H_e} - \widetilde{K}_{O_e}\right)\left(P - \sum P_{C_i}\right)$$

$$D \equiv -\,7\widetilde{K}_{O_e}\left(P - \sum P_{C_i}\right)$$

$$\lambda \equiv \widetilde{K}_{N_e} + \frac{28\,\widetilde{K}_{I_e}}{M_I} \tag{29}$$

After the cubic is solved, the partial pressure of H_2 is obtained from

$$P_{H_2} = \frac{28\widetilde{K}_{O_e}\left(P - \sum P_{C_i}\right) - \left(16\lambda + 28\widetilde{K}_{O_e}\right)P_{CO} - \left(32\lambda + 28\widetilde{K}_{O_e}\right)\alpha_9 P_{CO}^2}{28\widetilde{K}_{O_e} + \alpha_8\left(16\lambda + 28\widetilde{K}_{O_e}\right)P_{CO} + 28\alpha_{10}\widetilde{K}_{O_e}} \tag{30}$$

The carbon mass balance is solved for B' to yield

$$B' = -\,\widetilde{K}_{C_e} + \frac{B^*\left[P_{CO} + 2\alpha_{10}P_{H_2} + \alpha_9 P_{CO}^2 + \frac{1}{12}\sum M_{C_i}P_{C_i}\right]}{P_{CO} + 2\alpha_9 P_{CO}^2 + \alpha_8 P_{CO}P_{H_2}} \tag{31}$$

It should be emphasized that the result of Eq. (31) was obtained from the assumption that the surface recession is diffusion-controlled. In actual fact, at sufficiently low temperatures, the recession may be rate-limited. Therefore, Eq. (31) should be viewed as providing an upper bound for the recession at low temperatures.

After the calculation of B', the molecular weight may be calculated from one of the mass balances of Eq. (28). The hydrogen mass balance yields

$$\frac{PM}{1+B'}\tilde{K}_{H_e} = 2(1+\alpha_{10}+\alpha_8 P_{CO})P_{H_2} \qquad (32)$$

SECTION IV

COMPARISON WITH EXACT SOLUTIONS

In this section, the analytic solutions of Sections II and III are compared with exact results obtained from the ACE (Ref. 2) thermochemistry computer code. This code solves the general heterogeneous system, for a large number of species, with an iterative numerical scheme and is generally regarded as the standard of comparison in the reentry community.

Ideally, the comparisons between the ACE results and the present work should be carried out using identical assumptions and thermochemical data. Thus, the ACE results were generated using the option of equal diffusion coefficients. Two sources of thermochemical data [Horton (Ref. 3) and JANNAF (Ref. 4)] were used to generate the analytical solutions, whereas only JANNAF data are used in ACE. However, care was taken to insure that the data for the major species were identical to JANNAF. The slight differences among the secondary species are not significant enough to exert any impact on the mixture properties or mass transfer coefficient.

The first set of comparisons is for carbon sublimation in air and for comparison of the analytic solutions of Section II with ACE results. The values of Eq. (15) were used to represent air, and the first three carbon sublimation species were included in the analytic solution. Figures 1 and 2 show the mass loss coefficient (B') as a function of surface temperature for two pressures. The two solutions of Section II are shown as solid lines and indicate the influence of the carbon-nitrogen reactions on the mass transfer. The upper curve [Eq. (10)] includes all the dominant carbon-nitrogen reactions

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[3] Horton, T.E., and W.A. Menard, "A Program for Computing Shock-Tube Gas Dynamic Properties," Jet Propulsion Laboratory, Pasadena, California, TR-32-1350, January 1969.

[4] JANNAF Thermochemical Tables, National Bureau of Standards, NBS-37, June 1971.

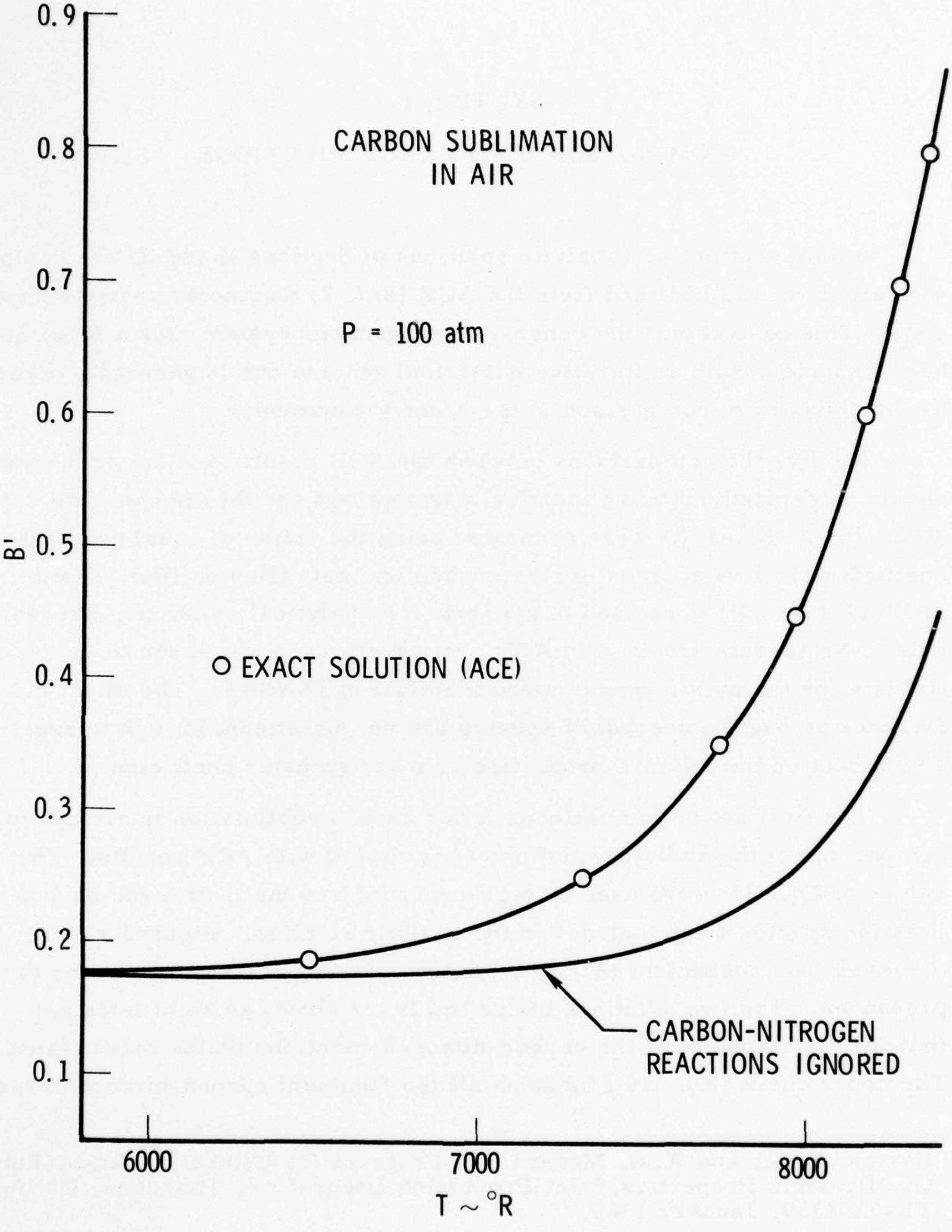

Fig. 1. Mass Transfer Parameter for Carbon Ablation in Air; P = 100 atm

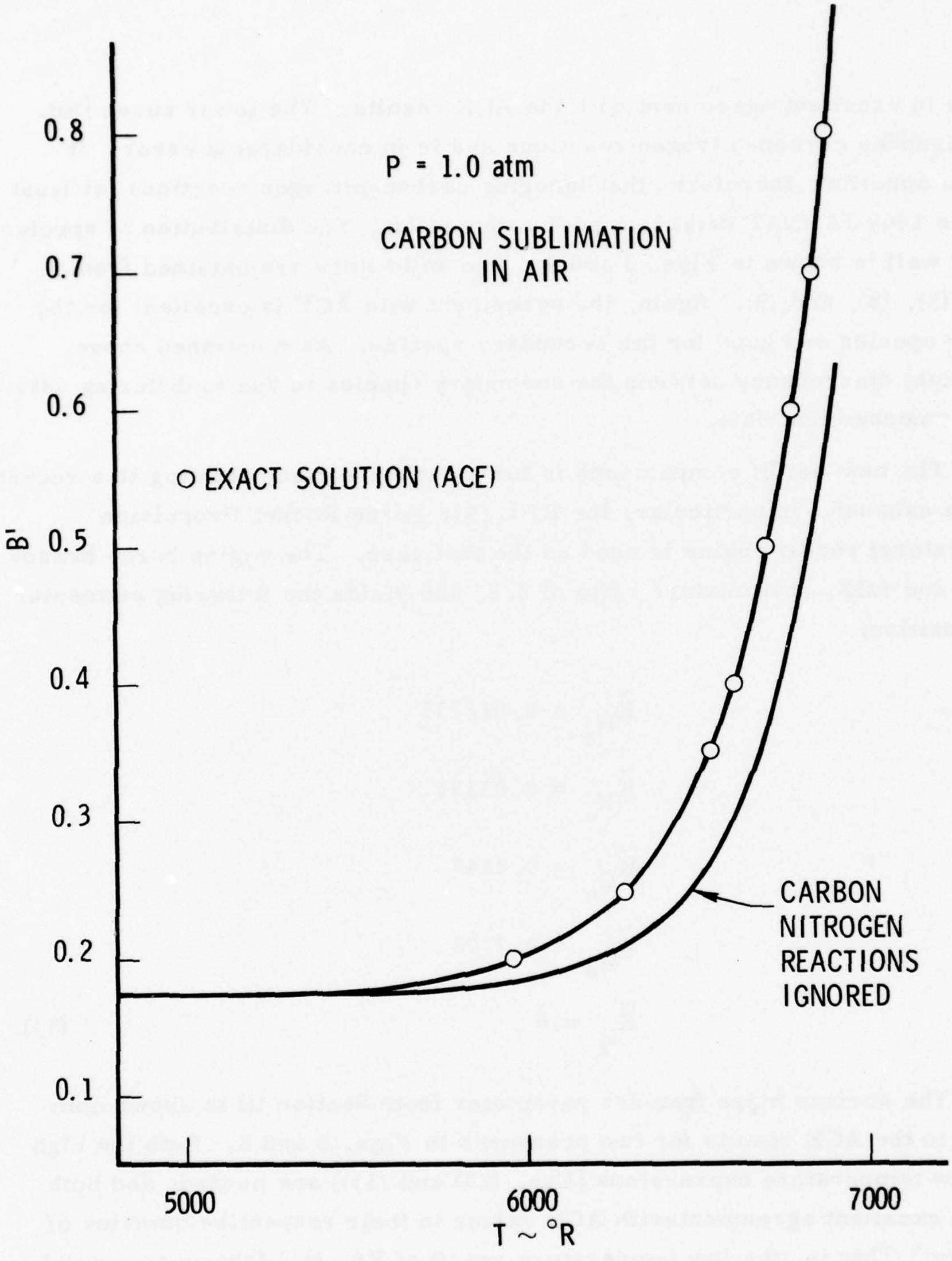

Fig. 2. Mass Transfer Parameter for Carbon Ablation in Air; P = 1.0 atm

and is in excellent agreement with the ACE results. The lower curve [Eq. (12)] ignores carbon-nitrogen reactions and is in considerable error. It seems apparent, therefore, that ignoring carbon-nitrogen reactions (at least for the 1969 JANNAF data) is a poor assumption. The distribution of species at the wall is shown in Figs. 3 and 4. The solid lines are obtained from Eqs. (5), (8), and (9). Again, the agreement with ACE is excellent for the major species and good for the secondary species. As mentioned above, the slight discrepancy between the secondary species is due to differing sets of thermochemical data.

The next set of comparisons is for a carbon surface ablating in a rocket engine exhaust. In particular, the RPL (Air Force Rocket Propulsion Laboratory) rocket engine is used as the test case. The engine burns benzoitrile and LOX, at a mixture ratio of 2.8, and yields the following elemental composition:

$$\begin{aligned} \tilde{K}_{H_e} &= 0.012755 \\ \tilde{K}_{N_e} &= 0.03571 \\ \tilde{K}_{C_e} &= 0.2143 \\ \tilde{K}_{O_e} &= 0.7372 \\ \tilde{K}_{I_e} &= 0 \end{aligned} \qquad (33)$$

The surface mass transfer parameter from Section III is shown compared to the ACE results for two pressures in Figs. 5 and 6. Both the high and low temperature expressions [Eqs. (23) and (31)] are plotted, and both are in excellent agreement with ACE values in their respective domains of validity. That is, the low temperature result of Eq. (31) (shown as a solid line) agrees well with the ACE results for low to moderate temperatures, and

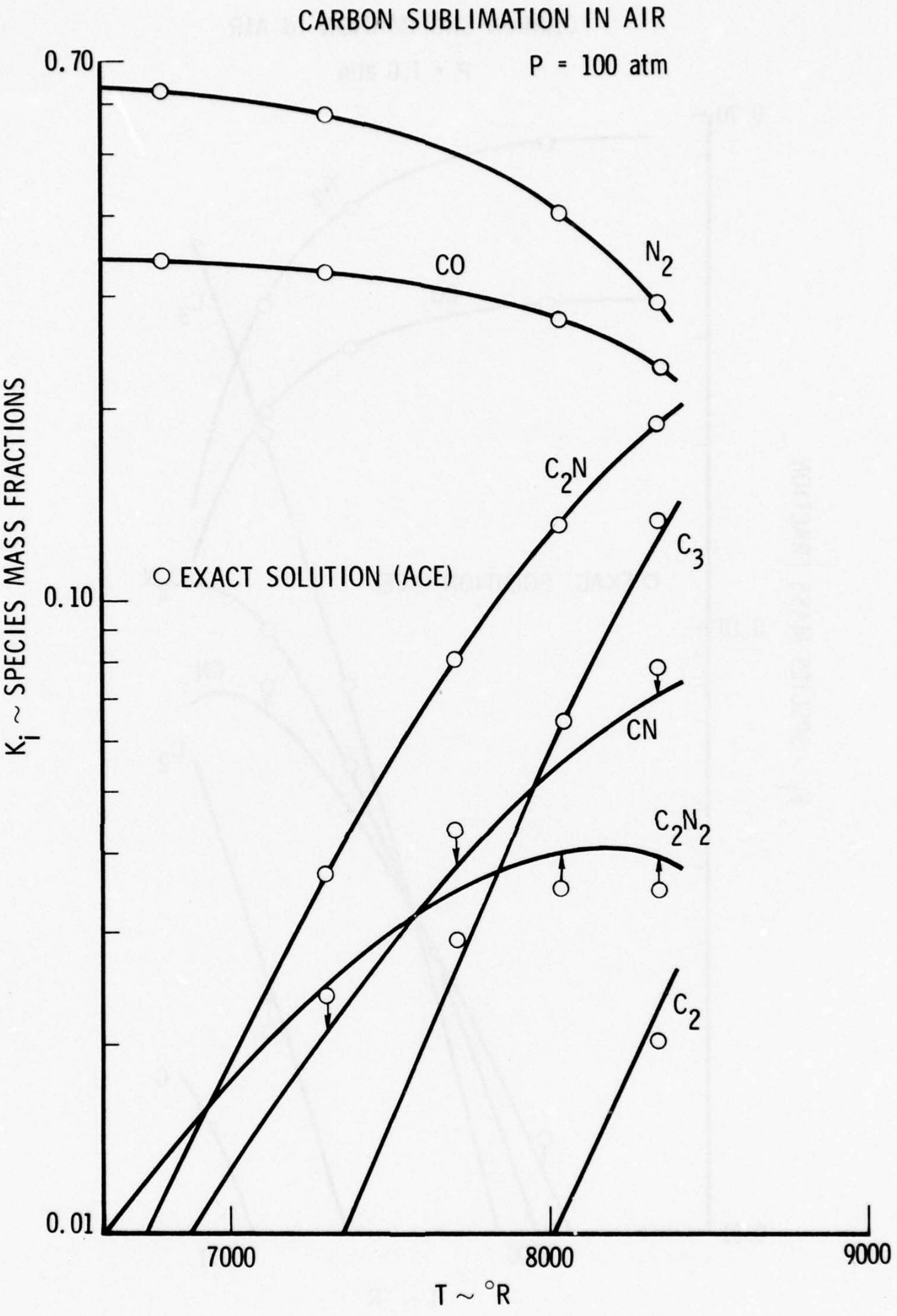

Fig. 3. Species Distribution at an Ablating Carbon Surface; P = 100 atm

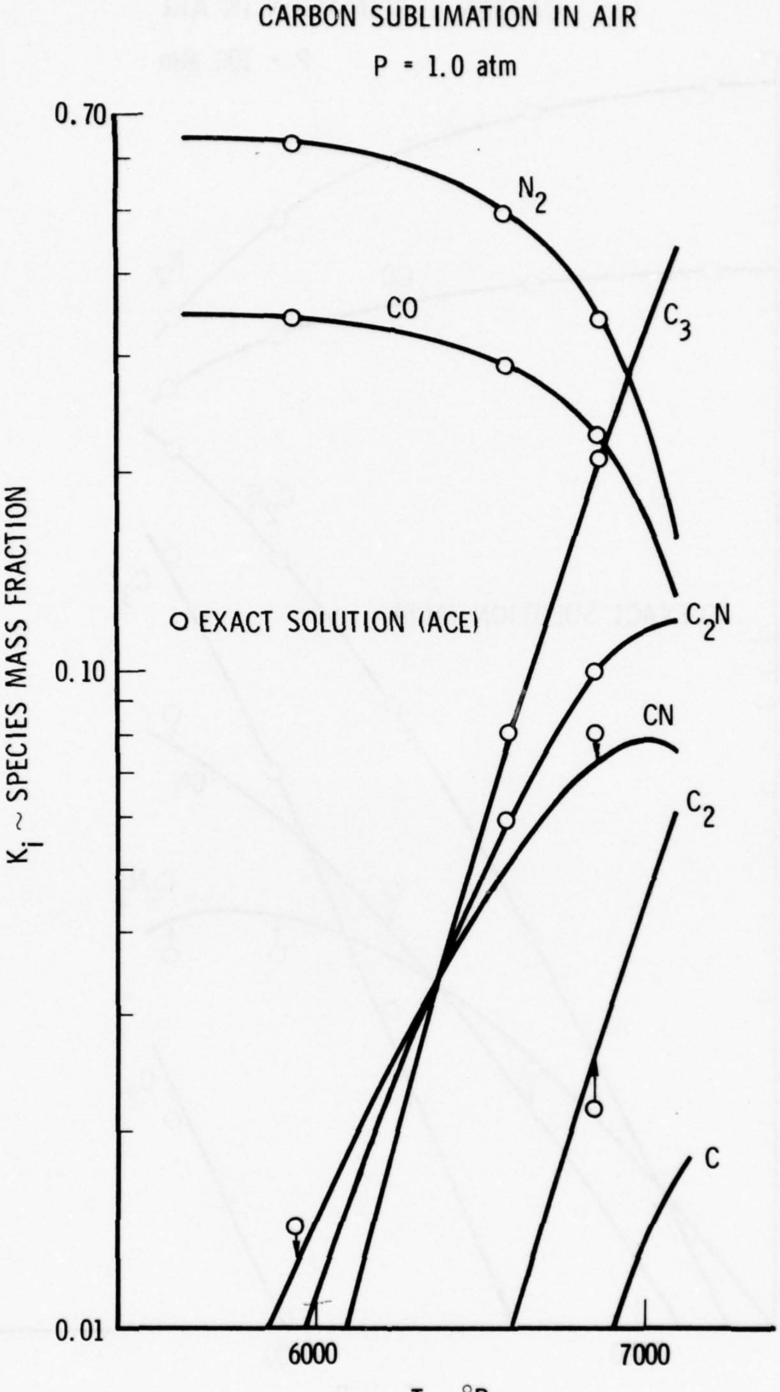

Fig. 4. Species Distribution at an Ablating Carbon Surface; P = 1.0 atm

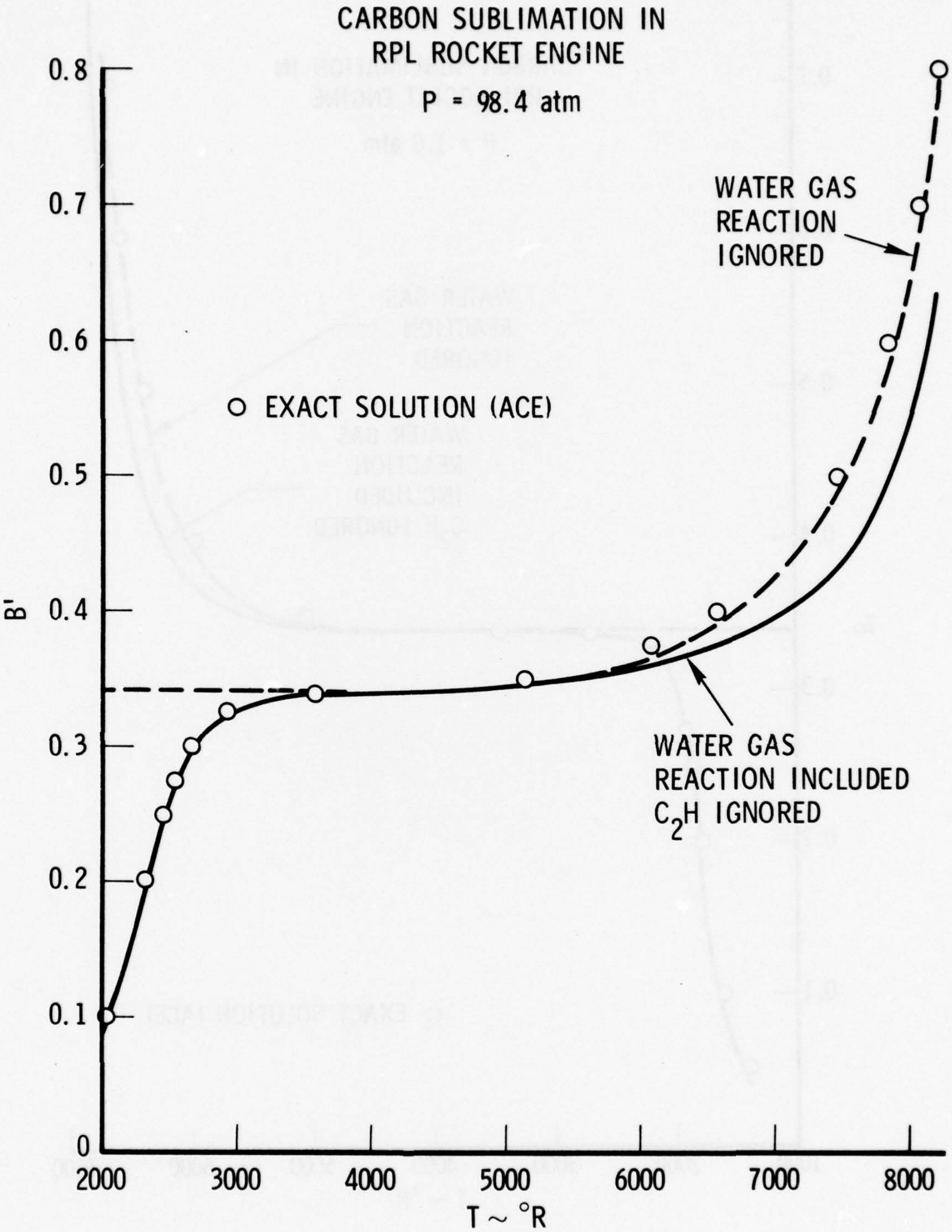

Fig. 5. Mass Transfer Parameter for Carbon Ablation in RPL Rocket Exhaust; P = 98.4 atm

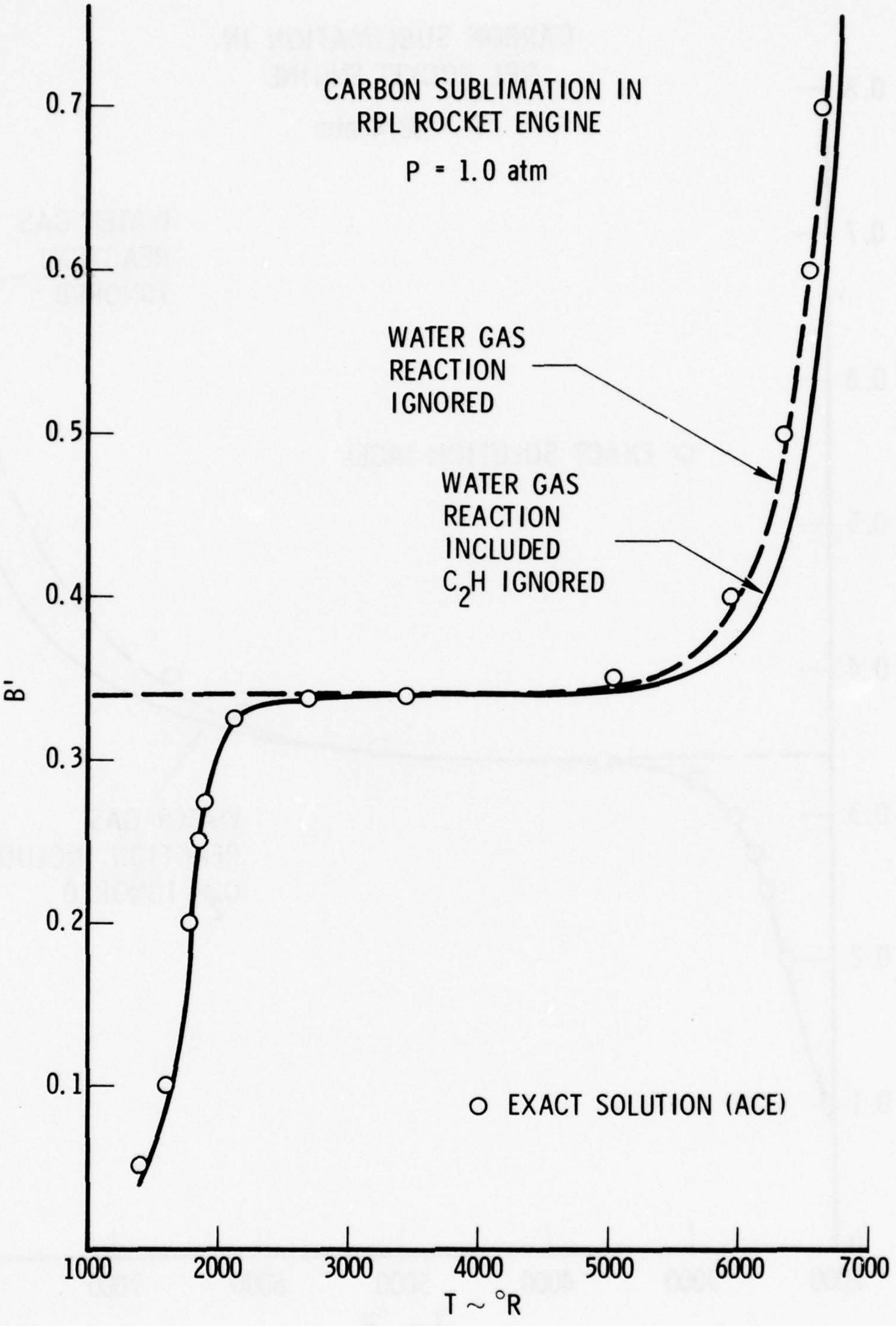

Fig. 6. Mass Transfer Parameter for Carbon Ablation in RPL Rocket Exhaust; P = 1.0 atm

the high temperature result of Eq. (23) (shown as a dashed line) is in good agreement for moderate to high temperatures. It is believed that the excellent agreement shown in Figs. 5 and 6 justifies the assumption that carbon-nitrogen reactions may be ignored relative to the carbon-hydrogen reactions. Notice that the low temperature result has the correct behavior at high temperatures, due to the inclusion of the carbon sublimation species, but does not rise fast enough because C_2H was ignored in the interests of obtaining an analytic solution.

The ACE results, in keeping with the assumptions of this report, are all for diffusion-controlled surface reactions. Thus, at low temperatures, where the reactions may be rate limited, the results of Figs. 5 and 6 should be interpreted as upper bounds to the actual recession rate.

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SECTION V

SUMMARY AND CONCLUSIONS

A new class of analytic solutions has been presented for mass transfer from a carbon surface subliming into atmospheres of varying elemental composition. The solutions are computationally trivial, requiring only the evaluation of a single quadratic equation (in the diffusion limited regime) and are in excellent agreement with exact results generated by the ACE code.

For an atmosphere of elemental C-N-O-I, a single analytic solution for B' was obtained in the temperature regime where the oxidation reaction is diffusion-limited. An arbitrary number of carbon sublimation species is included in the solution, as well as all the dominant carbon-nitrogen reactions.

When hydrogen is added to the elemental composition, the analytic solution is achieved by ignoring carbon-nitrogen reactions and treating the dominant carbon-hydrogen reactions. Two solutions are presented for this case: one valid in the temperature domain where the oxidation reaction is diffusion-limited and a second valid at lower temperatures where the water gas reaction is dominant.

The solutions should be particularly suited for applications in which the atmospheric elemental composition is frequently changed and in situations where a knowledge of the analytic behavior of B' with temperature is desired.

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APPENDIX A

VAPOR PRESSURE OF CARBON SUBLIMATION SPECIES

As discussed in the main text (Section II), the vapor pressure of each gaseous carbon species is assumed to be a known function of temperature. These vapor pressures are presented in this appendix.

The gaseous carbon species in equilibrium with the solid carbon surface are denoted by C_i. The vaporization reaction is given as

$$i\,C_{solid} \rightarrow C_i \tag{A-1}$$

For this reaction, the third law gives

$$\ell n\, P_{C_i} = \frac{-E_0(C_i)}{RT} - \left(\frac{F^0 - H_0^0}{RT}\right)_{C_i} + i\left(\frac{F^0 - H_0^0}{RT}\right)_{solid} \tag{A-2}$$

where $E_0(C_i)$ is the heat of formation of C_i at 0^oK and the heat of formation of solid carbon has been set equal to zero by convention.

The free-energy function and partition function for the gaseous species are related as follows:

$$\left(\frac{F^0 - H_0^0}{RT}\right)_{C_i} = -\,\ell n\, Q_P(C_i) \tag{A-3}$$

The free-energy function is related to the specific heat by

$$\frac{F^0 - H_{298}^0}{T} = \frac{1}{T}\int_{298}^{T} C_p\, dT - \int_{298}^{T} \frac{C_p}{T}\, dT - S_{298}^0 \tag{A-4}$$

Note that the JANNAF (Ref. 4) thermochemical data uses a base temperature of 298°K. The free-energy functions at 0°K and 298°K are related by

$$\frac{F^0-H_0^0}{T} = \frac{F^0-H_{298}^0}{T} - \frac{H_0^0-H_{298}^0}{T} \tag{A-5}$$

The free-energy function referenced to 298°K and the difference in enthalpies between 0°K and 298°K are both tabulated in JANNAF.

For solid carbon, the JANNAF data yields

$$\frac{F^0-H_0^0}{T} = \frac{F^0-H_{298}^0}{T} + \frac{252}{T} \tag{A-6}$$

The curve fits for specific heat in the ACE (Ref. 2) code were used to evaluate the free-energy function for solid carbon by using Eq. (A-4). The final result is

$$\frac{F^0-H_{298}^0}{T} = A(1-\ell nT) - \frac{1}{2}BT - \frac{C}{2T^2} - \frac{D}{T} + E \tag{A-7}$$

$T \leq 3000$°K:

$A = 5.861$
$B = 0.954 \times 10^{-4}$
$C = -0.7666 \times 10^6$
$D = 4323.3$
$E = 35.235$

$T \geq 3000^{\circ}K$:

$A = 4.85$
$B = 0.2916 \times 10^{-3}$
$C = 0.3072 \times 10^{7}$
$D = 893.7$
$E = 27.516$

where all temperatures are in degrees Kelvin and the units of the free-energy functions are cal/mol-°K.

The use of Eqs. (A-6) and (A-7) in Eq. (A-2) provides all the necessary information about the solid phase.

The partition functions were used to obtain the free-energy function for C and C_2 and are presented in Appendix B. The C_3 free-energy function was again obtained from the specific heat curve fit in the ACE code (1969 JANNAF). The C_3 free-energy function is identical to the form of Eq. (A-7) with the following values for the constants:

$$H_0^0 - H_{298}^0 = -2811 \text{ cal/mol}$$

$T \leq 2500^{\circ}K$:

$A = 10.223$
$B = 1.0066 \times 10^{-3}$
$C = -0.44592 \times 10^{6}$
$D = 4587.525$
$E = 3.722$

$T \geq 2500^{\circ}K$:

$A = 12.524$
$B = 2.3055 \times 10^{-4}$
$C = -0.27025 \times 10^{7}$
$D = 8817.501$
$E = 19.966$

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APPENDIX B

EQUILIBRIUM CONSTANTS

This appendix contains the necessary information required to calculate the pressure equilibrium constants which are used in the main text.

The reactions considered are all of the following form:

$$a_1 A_1 + a_2 A_2 \rightarrow b_1 B_1 + b_2 B_2 \tag{B-1}$$

where the A_i are the reactants and the B_i the products. The equilibrium constant for this reaction is defined in terms of the partial pressures as

$$K_P = \frac{P_{B_1}^{b_1} \; P_{B_2}^{b_2}}{P_{A_1}^{a_1} \; P_{A_2}^{a_2}} \tag{B-2}$$

where P_{A_1} denotes the partial pressure of A_1.

The equilibrium constant may be computed from a knowledge of the partition function (or equivalently, the free energy function) of each species involved in the reaction. That is

$$\log K_P = \frac{-\Delta E_0}{RT} + b_1 \log Q_p (B_1) + b_2 \log Q_p (B_2)$$

$$- a_1 \log Q_p (A_1) - a_2 \log Q_p (A_2)$$

$$\Delta E_0 = b_1 E_0 (B_1) + b_2 E_0 (B_2) - a_1 E_0 (A_1) - a_2 E_0 (A_2) \tag{B-3}$$

where E_0 is the heat of formation at 0°K.

The equilibrium constants are defined for the indicated reactions as follows:

$$K_{P_1}\,(N_2 + 2C \rightarrow 2\;CN)$$

$$K_{P_2}\,(C_2N_2 \rightarrow 2\;CN)$$

$$K_{P_3}\,(C_4N_2 \rightarrow 2\;CN + 2C)$$

$$K_{P_4}\,(C_2N \rightarrow CN + C)$$

$$K_{P_5}\,(C_2H \rightarrow H + 2C)$$

$$K_{P_6}\,(C_2H_2 \rightarrow 2H + 2C)$$

$$K_{P_7}\,(H_2 \rightarrow 2H)$$

$$K_{P_8}\;H_2O + CO \rightarrow CO_2 + H_2)$$

$$K_{P_9}\,(C + CO_2 \rightarrow 2\;CO)$$

$$K_{P_{10}}\,(C_2H_2 \rightarrow H_2 + 2C) \tag{B-4}$$

The heat of reaction term is defined for each reaction as follows:

K_P	$\Delta E_0/R \sim {}^oK$
1	-67260.0
2	66993.0
3	211521.0
4	71143.0
5	138419.0
6	195816.0
7	51984.0
8	-4861.0
9	-65687.0
10	143832.0

The partition functions used in this report were obtained from the data of Horton (Ref. 3) and JANNAF (Ref. 4) and are given in Table B-1. The C_3 partition function may be calculated from the free energy functions presented in Appendix A. Similarly, the free energy function for C_4N_2 is also obtained from **Eqs.** (A-5) and (A-7) of Appendix A, with the following constants.

$$H_0^0 - H_{298}^0 = -4239 \text{ cal/mol}$$

$T \leq 2500^oK$:

A = 28.903

B = 0.13659×10^{-2}

C = -0.14872×10^{7}

D = 1.3664×10^{4}

E = 102.664

$T \geq 2500^{\circ}K$:

$A = 32.053$

$B = 0.109 \times 10^{-3}$

$C = -0.15347 \times 10^{7}$

$D = 1.7631 \times 10^{4}$

$E = 124.171$

Table B-1. Partition Functions

$$\log Q_p(C) = 2.5 \log T + 0.07 + \log [9 + 5 \exp(-14667/T) + \exp(-31147/T)]$$

$$\log Q_p(N_2) = 3.5 \log T - 0.41 - \log [1 - \exp(-3372/T)]$$

$$\log Q_p(CO) = 3.5 \log T + 0.32 - \log [1 - \exp(-3103/T)]$$

$$\log Q_p(C_2N_2) = 3.5 \log T + 3.04 - 2 \log [1 - \exp(-325/T)] - 2 \log [1 - \exp(-728/T)] - \log [1 - \exp(-1220/T)]$$
$$- \log [1 - \exp(-3092/T)] - \log [1 - \exp(-3341/T)]$$

$$\log Q_p(CO_2) = 3.5 \log T + 1.90 - 2 \log [1 - \exp(-960/T)] - \log [1 - \exp(-1932/T)] - \log [1 - \exp(-3880/T)]$$

$$\log Q_p(H_2) = 3.5 \log T - 7.759 - \log [1 - \exp(-6154/T)]$$

$$\log Q_p(H) = 2.5 \log T - 2.9658$$

$$\log Q_p(C_2H) = 3.5 \log T + 1.8215 - \log [1 - \exp(-2767/T)] - \log [1 - \exp(-4629/T)] - 2 \log [1 - \exp(-1024/T)]$$

$$\log Q_p(C_2H_2) = 3.5 \log T + 0.0087 - \log [1 - \exp(-4852/T)] - \log [1 - \exp(-2839/T)] - \log [1 - \exp(-4731/T)]$$
$$- 2 \log [1 - \exp(-1049/T)] - 2 \log [1 - \exp(-881/T)]$$

$$\log Q_p(C_2N) = 3.5 \log T + 2.918 - \log [1 - \exp(-1727/T)] - \log [1 - \exp(-1295/T)] - 2 \log [1 - \exp(-462/T)]$$

$$\log Q_p(H_2O) = 4 \log T - 4.106 - \log [1 - \exp(-5262/T)] - \log [1 - \exp(-2294/T)] - \log [1 - \exp(-5404/T)]$$

$$\log Q_p(C_2) = 3.5 \log T + 0.4149 + \log \Big[1/[2.606 - 2.606 \exp(-2649/T)] + 6 \exp(-878/T)/[2.338 - 2.338 \exp$$
$$(-2345/T)] + 3 \exp(-8983/T)/[2.145 - 2.145 \exp(-2100/T)] + 2 \exp(-11896/T)/[2.313 -$$
$$2.313 \exp(-2297/T)] + 2 \exp(-14388/T)/[2.127 - 2.127 \exp(-2115/T)]\Big]$$

$$\log Q_p(CN) = 3.5 \log T + 1.147 + \log \Big[2.0/[2.72 - 2.72 \exp(-2958/T)] + 4 \exp(-13114/T)/[2.46 - 2.46 \exp$$
$$(-2592/T)]\Big]$$

APPENDIX C

DETAILS OF THE ANALYTIC SOLUTION

The algebraic operations leading to Eqs. (9) and (10) of Section II are presented in this appendix.

As indicated in the text, Eq. (3) is cast in terms of partial pressures by multiplying through by the product of pressure and molecular weight. This operation, in conjunction with the use of Eq. (7), yields the following:

$$\frac{PM}{1+B'}\tilde{K}_{O_e} = 16\,P_{CO}$$

$$\frac{PM}{1+B'}\tilde{K}_{N_e} = 28\,P_{N_2} + 14\,P_{CN} + 28\,P_{C_2N_2} + 28\,P_{C_4N_2} + 14\,P_{C_2N}$$

$$\frac{PM}{1+B'}\left(B' + \tilde{K}_{C_e}\right) = 12\,P_{CO} + 12\,P_{CN} + 24\,P_{C_2N_2} + 48\,P_{C_4N_2} + 24\,P_{C_2N} + \sum M_{C_i}P_{C_i}$$

$$\frac{PM}{1+B'}\tilde{K}_{I_e} = M_I P_I \qquad \text{(C-1)}$$

The sum of the partial pressures must equal the mixture pressure. That is

$$P = P_{CO} + P_{N_2} + P_{CN} + P_{C_2N_2} + P_{C_4N_2} + P_{C_2N} + P_I + \sum P_{C_i} \qquad \text{(C-2)}$$

Substitution of P_{CO} and P_I from Eq. (C-1) into Eq. (C-2) yields

$$\frac{MP}{1+B'}\left[\frac{\tilde{K}_{O_e}}{16}+\frac{\tilde{K}_{I_e}}{M_I}\right] = P - \sum P_{C_i} - P_{N_2} - P_{CN}$$

$$- P_{C_2N_2} - P_{C_4N_2} - P_{C_2N} \qquad \text{(C-3)}$$

Combining Eq. (C-3) with the nitrogen mass balance of Eq. (C-1) yields

$$(28\lambda+1)\left(P_{N_2} + P_{C_2N_2} + P_{C_4N_2}\right) +$$

$$+ (14\lambda+1)\left(P_{CN} + P_{C_2N}\right) = P - \sum P_{C_i} \qquad \text{(C-4)}$$

Substitution of the equilibrium relationships of Eq. (5) into Eq. (C-4) yields the result of Eq. (9).

Substitution of P_{CO} into the carbon mass balance of Eq. (C-1) yields

$$\frac{PM}{1+B'}\left(B' + \tilde{K}_{C_e} - B^*\right) = 12\ P_{CN} + 24\ P_{C_2N_2} + 48\ P_{C_4N_2} +$$

$$+ 24\ P_{C_2N} + \sum M_{C_i} P_{C_i} \qquad \text{(C-5)}$$

The term $PM/(1+B')$ may be eliminated from Eq. (C-5) by using either Eq. (C-3) or the nitrogen mass balance of Eq. (C-1). Equation (10) was obtained by using the latter and the equilibrium expressions of Eq. (5).

APPENDIX D

GENERALIZED ANALYSIS OF THE C-N-O-I SYSTEM

The analysis of Section II ignored the presence of CO_2 at the wall and assumed that all the oxygen was bound in CO. This limits the validity of the results to surface temperatures high enough to preclude the formation of CO_2. As mentioned on page 14, at the low surface temperatures required for the existence of CO_2 the surface recession is likely to be rate limited, and the diffusion-controlled calculation provides only an upper bound to the actual recession. There are, however, situations in which a knowledge of the upper bound recession suffices, and the complexity of the surface kinetic reactions may be ignored. In order to obtain a reasonable upper bound value for B', the CO_2 reaction must be included in the formulation. It is the purpose of this appendix to generalize the analysis of Section II by including CO_2 in the formulation.

The analysis is considered below in two parts. In the first part, the problem is formulated and discussed. Since the generalized formulation leads to a quartic equation (which is time consuming to evaluate), an approximate (but very accurate) method of solution is presented in part 2.

1. FORMULATION

The reactions include those of Eq. (2) plus the CO_2 reduction reaction which is given as

$$C + CO_2 \rightarrow 2\,CO \qquad \text{(D-1)}$$

The equilibrium relationships include those of Eq. (5) as well as the relation between the CO and CO_2 partial pressures.

$$P_{CO_2} = \alpha_5 P_{CO}^2 \qquad \alpha_5 \equiv \frac{1}{P_C K_{P_5}} \qquad \text{(D-2)}$$

Note that the α_5 coefficient of Eq. (D-2) is not the same as that of Eq. (21).

The elemental mass balances of Eq. (3) have the additional terms added as follows:

$$\tilde{K}_{O_W} = \frac{16}{28} K_{CO} + \frac{32}{44} K_{CO_2}$$

$$\tilde{K}_{C_W} = \frac{12}{28} K_{CO} + \frac{12}{44} K_{CO_2} + \frac{12}{26} K_{CN} + \frac{24}{52} K_{C_2N_2} + \frac{48}{76} K_{C_4N_2} + \frac{24}{38} K_{C_2N} + \sum K_{C_i} \qquad \text{(D-3)}$$

The nitrogen and inert elemental mass balances of Eq. (3) are unchanged.

The molecular weight Eq. (4) becomes

$$\frac{1}{M} = \frac{K_{CO}}{28} + \frac{K_{CO_2}}{44} + \frac{K_{N_2}}{28} + \frac{K_{CN}}{26} + \frac{K_{C_2N_2}}{52} + \frac{K_{C_4N_2}}{76} + \frac{K_{C_2N}}{38} + \frac{K_I}{M_I} + \sum \frac{K_{C_i}}{M_{C_i}} \qquad \text{(D-4)}$$

Equations (7), relating the wall and boundary layer edge elemental mass fractions, are unchanged.

In the same manner as in Section II, the set of equations may be manipulated to yield the following equations for the partial pressures of CO and CN.

$$(\alpha_1 + \alpha_2 + \alpha_3)P_{CN}^2 + \frac{1}{2}(1 + \alpha_4)P_{CN} = 16\lambda_1 P_{CO} + 32\lambda_1 \alpha_5 P_{CO}^2$$

$$\lambda_1 \equiv \frac{\tilde{K}_{N_e}}{28\,\tilde{K}_{O_e}} \qquad \lambda_2 \equiv \frac{\tilde{K}_{I_e}}{M_I \tilde{K}_{O_e}} \qquad \text{(D-5)}$$

$$(32\lambda_2 + 1)\alpha_5 P^2_{CO} + (16\lambda_2 + 1)P_{CO} = P - \sum P_{C_i} +$$

$$- (\alpha_1 + \alpha_2 + \alpha_3)P^2_{CN} - (1 + \alpha_4)P_{CN} \qquad \text{(D-6)}$$

Equations (D-5) and (D-6) may be combined to yield a quartic for the partial pressure of CO. After the quartic is solved, the CN partial pressure is calculated from Eq. (D-5) and the remaining partial pressures are obtained from Eqs. (5) and (D-2). Following the determination of the partial pressures, the molecular weight and B' are calculated from Eqs. (D-3) (recast in terms of partial pressures). These equations yield

$$\frac{PM}{1+B'} \tilde{K}_{O_e} = 16\ P_{CO} + 32\ P_{CO_2}$$

$$\frac{PM}{1+B'} \left(B' + \tilde{K}_{C_e}\right) = 12\ P_{CO} + 12\ P_{CO_2} + 12\ P_{CN} + 24\ P_{C_2N} +$$

$$+ 24\ P_{C_2N_2} + 48\ P_{C_4N_2} + \sum M_{C_i} P_{C_i} \qquad \text{(D-7)}$$

This completes the generalization of the analysis of Section II to include the dominant low temperature reaction [i.e., Eq. (D-1)].

A comment is in order concerning the advisability of including O_2 among the low temperature reactions. That is, it is quite easy to add an additional reaction specifying equilibrium between C, CO and O_2 (or, equivalently, O_2, CO_2 and CO) and including O_2 in the oxygen elemental balance of Eq. (D-3) and the molecular weight equation, (D-4). Inclusion of O_2 in the analysis changes only the coefficients of the quadratic terms involving the CO partial pressure of Eqs. (D-5) and (D-6). Calculations were done with the O_2 included, and it was found to exert no influence on the results down to temperatures as low as 600°R. Therefore, it was deleted in the above description of the analysis.

The limiting behavior of the mass transfer parameter B' for large and small temperatures is considered next. Since O_2 was ignored in the analysis, as the temperature vanishes, only CO_2 is present at the wall and B' approaches a constant value. That is

T→0 (CO_2 plateau):

$$B' = \frac{12}{32} \tilde{K}_{O_e} - \tilde{K}_{C_e}$$

$$B' = 0.087 \text{ for air} \tag{D-8}$$

where the values of Eq. (15) were used for air. In contrast, the low temperature limit for the analysis of Section II (where only CO is present as the temperature vanishes) is given as

T→0 (CO plateau):

$$B' = \frac{12}{16} \tilde{K}_{O_e} - \tilde{K}_{C_e}$$

$$B' = 0.174 \text{ for air} \tag{D-9}$$

There exists an upper limit temperature beyond which no equilibrium solution exists. This limiting temperature is a function of pressure and is defined by the sum of the carbon vapor pressures equal to the mixture pressure. This yields

$$\sum P_{C_i} (T_{limit}) = P \tag{D-10}$$

The high temperature behavior of the generalized system is identical to that of Section II and is given as

$T \rightarrow T_{\text{limit}}$:

$$P_{CN} = \frac{P - \sum P_{C_i}}{(1 + 14\lambda)(1 + \alpha_4)} \longrightarrow 0$$

$$P_{CO} = \frac{14\, B^* \left(P - \sum P_{C_i}\right)}{12(1 + 14\lambda)\tilde{K}_{N_e}} \longrightarrow 0$$

$$B' = \frac{\tilde{K}_{N_e}(1 + 14\lambda)\sum M_{C_i} P_{C_i}}{14\left(P - \sum P_{C_i}\right)} \longrightarrow \infty \qquad \text{(D-11)}$$

where λ is defined by Eq. (9).

2. SOLUTION

As indicated above, Eqs. (D-5) and (D-6) may be combined to yield a quartic for the CO (or CN) partial pressure. Although an analytic solution exists for a quartic, it is time consuming to evaluate, and the possibility of more than one plausible root complicates the issue. In order to avoid this complexity, the solution for the CO partial pressure is split into high- and low-temperature regimes requiring only the solution of a quadratic in each regime.

In the low temperature regime, the carbon-nitrogen species are ignored and the following quadratic is obtained.

$$\alpha_5(1 + 32\lambda_1 + 32\lambda_2)P_{CO}^2 + (1 + 16\lambda_1 + 16\lambda_2)P_{CO} + {} - \left(P - \sum P_{C_i}\right) = 0 \qquad \text{(D-12)}$$

There is only one positive root, and it is obtained by using the positive radical in the quadratic solution.

The high temperature solution for P_{CO} is obtained from the results of Section II. That is, after solving Eq. (9) for P_{CN}, the CO partial pressure is calculated from

$$P_{CO} = \frac{\tilde{K}_{O_e}}{16\,\tilde{K}_{N_e}} \left[28(\alpha_1 + \alpha_2 + \alpha_3)P_{CN}^2 + 14(1 + \alpha_4)P_{CN} \right] \qquad \text{(D-13)}$$

The correct value for P_{CO}, for any temperature, will be the smaller of the two values obtained from Eqs. (D-12) and (D-13). After obtaining this value for P_{CO}, Eq. (D-5) is solved as a quadratic for the CN partial pressure, and the remaining partial pressures are calculated from Eqs. (D-2) and (5). Then Eqs. (D-7) are solved for B' and the molecular weight.

In this manner, an approximate solution is obtained for the generalized formulation without the need to evaluate a quartic equation. The solution is continuous for all temperatures and is quite accurate.

The calculations of Section II for an ablating carbon surface in air were recalculated with the analysis of this appendix over a much wider temperature range. At high temperatures, the results were identical to those shown in Figs. 1 through 4. The low temperature results for B' are compared in Fig. D-1 with solutions from the ACE (Ref. 2) computer code. Again, the agreement is excellent.

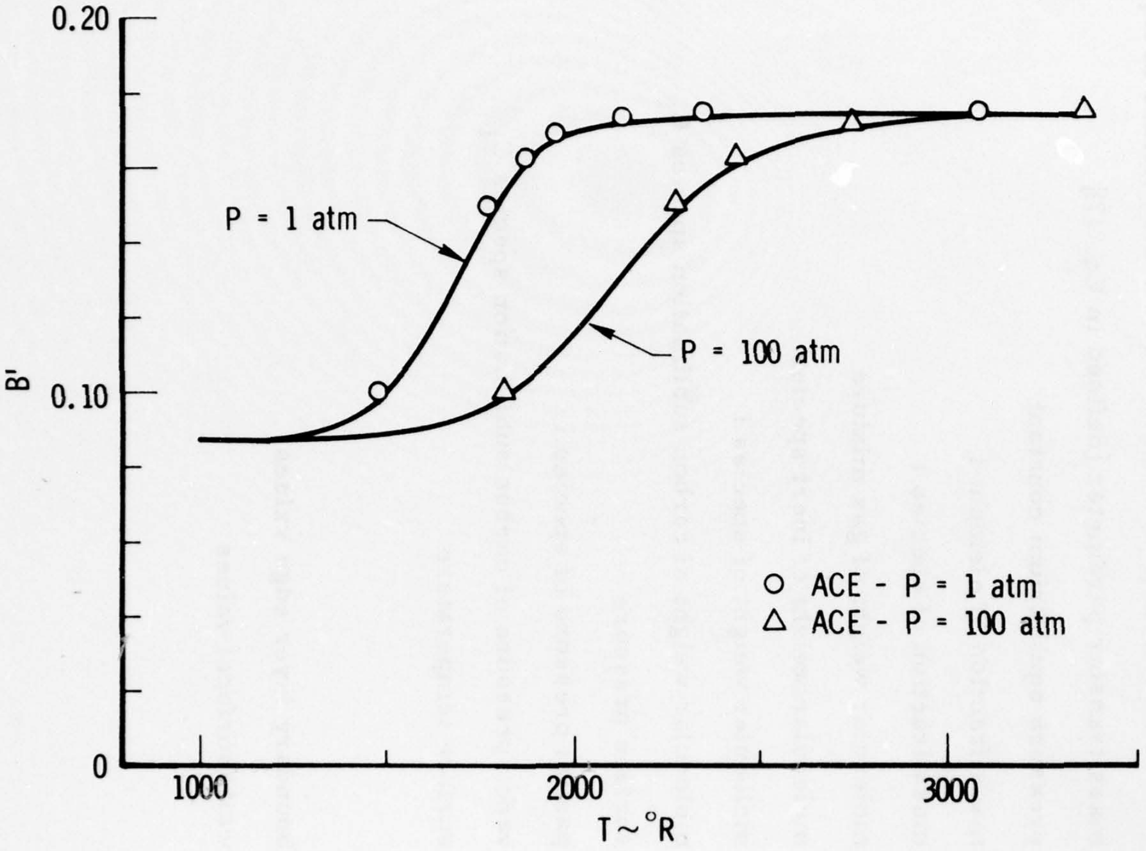

Fig. D-1. Carbon Sublimation in Air

NOMENCLATURE

B^*	diffusion limited mass transfer coefficient [defined in Eq. (10)]
B'	mass transfer parameter [defined in Eq. (7)]
K_P	pressure equilibrium constant
$\tilde{K}_i$	mass fraction of element i
K_i	mass fraction of species i
M	molecular weight of gas mixture
M_I	molecular weight of inert species
M_i	molecular weight of species i
M_{c_i}	molecular weight of carbon sublimation species C_i
P	surface pressure
P_i	partial pressure of species i
P_{c_i}	vapor pressure of carbon sublimation species C_i
T	surface temperature

Subscripts

e	boundary layer edge values
w	wall (surface) values

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