of these materials are very unlikely. Since the reaction takes place only at the surface, the Damköhler number appears only in the surface boundary condition. In the flowfield the Damköhler number is zero. When the Arrhenius rates, given for such materials are used, the Damköhler number is strongly dependent on surface temperature and only weakly on time. It is well known that the similarity solution of the type used in Ref. 1 is not valid for $t = 0$. When moderate values of t are considered, the Damköhler number is well behaved (monotonically). So, even in the transitional regime where the essential parametric variation is in the surface temperature, the results based on this quasi-steady boundary condition remained meaningful if they are interpreted consistent with the surface boundary condition of Eq. (13) of Ref. 1. In the diffusion-limited regime this boundary condition is well defined regardless of surface temperature or time, and so are the corresponding results. It is true that these solutions do not provide the exact time history of the reaction path. Such results were not intended in the studies of Ref. 1. The result for equilibrium surface temperature, however, is well defined by that study.

It is further pointed out that our consideration of system stability is based on the surface heat and mass balance and is not the same as that of the multiple solutions in nonequilibrium gaseous combustion analyses (Refs. 4 and 5 of the preceding Note). In the latter analyses, the multiple solutions are a result of local excursion of the Damköhler numbers in the flowfield. A more valid comparison with our analysis is to Spalding's work noted in Ref. 1, in which system stability had been considered in a similar manner for the surface combustion of carbon in a convective flow. References 6 and 8 of the preceding Note are not yet in the open literature; it is therefore not possible at this writing to include their merits in the discussion.

Then, for the purposes intended, the analyses and results of Ref. 1 are valid. As in many examples of boundary layer and related studies, solutions using local similarity and using the complete partial differential system each has its own merits, depending on the nature of problem in question. Different approaches often aid the over-all understanding. It is in part under such a premise that the results of Ref. 1 were offered.

Comment on "Chemistry of Electrons in Pure-Air Hypersonic Wakes"

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Introduction

Measurements of the electron line densities appearing in the wakes of hypersonic pellets[1] have provided stimulus for concomitant theoretical computations which are designed to test suitable chemical-gas-dynamical wake models. In the model adopted recently by Sutton,[2] related to earlier work of Lin and Hayes,[4] a chemically reacting laminar flowfield obtained by the streamtube method for a sphere with suitably streamlined afterbody (to avoid the difficulties associated with the details of base flow) is used to calculate input specie flux densities to a wake that assumes the one-third-power-with-distance radius growth law[5] and an infinite viscous dissipation rate. We refer the reader to the articles of Lin and Hayes,[4] Sutton,[2] and others,[7–10] for full discussion of this homogeneous mixing model and of other pertinent wake phenomena.

The purpose of the present comment is to draw attention to a possibly significant difference between the homogeneous mixing model employed by Sutton[2] and the original homogeneous mixing model examined by Lin and Hayes,[4] and to the presence of possible internal inconsistencies in the computational results so obtained. In addition, we question the general legitimacy of Sutton's application of the homogeneous mixing model to problems in wake chemistry by drawing attention to a number of features of the model which are apparently incompatible with observation.

Homogeneous Mixing

Restricting our attention to the far wake, subsequent to breakthrough,[6] we have from Lin and Hayes,[4]

$$\left.\frac{dn_i}{dt}\right|_{\text{mixing}} = \frac{2}{3}\,[n_i(\infty) - n_i(t)]t^{-1} \tag{1}$$

for the time rate of change due to ingestion and wake expansion of the number density, $n_i(t)$, of the ith wake specie, where $n_i(\infty)$ is the ith specie ambient number density. On the other hand, we have from Sutton [Ref. 3, Eq. (21), correcting a typographical error], for the same mixing derivative,

$$\left.\frac{dn_i}{dt}\right|_{\text{mixing}} = n(t)\,\frac{n_i(\infty)}{n(\infty)}\left(\frac{2}{3}\,t^{-1} - \frac{1}{T}\,\frac{dT}{dt}\right) - \frac{2}{3}\,n_i(t)t^{-1} \tag{2}$$

where $n(t)$ and $n(\infty)$ are the wake and ambient total number densities, respectively. Here, Eq. (1) follows from consideration of the derivative of $n_i(t) = N_i(t)/V(t)$, with dN_i/dt (ingestion) $= n_i(\infty)dV/dt$ where the change in wake reference volume is determined by the one-third-power-with-distance wake radius growth law.[5] Equation (2) follows from similar consideration with, however, dN_i/dt (ingestion) $= [n_i(\infty)/n(\infty)]dN/dt$, where the rate of change of the total number of wake particles, dN/dt, in the reference volume $V(t)$ is determined in terms of temperature and volume changes by the ideal gas law. The latter procedure is an approximation and evidently assumes that the rate of change of wake particles due to chemical reaction is negligibly smaller than the particle ingestion rate due to wake expansion.

We now examine the conditions under which the mixing rates of Eqs. (1) and (2) can differ. Such difference will evidently depend on the manner in which the temperature history, $T(t)$, in Eq. (2) is obtained. Following Sutton, this temperature history can be determined by equating the rate of change of wake enthalpy per unit length to the ingested enthalpy plus that produced by chemical reaction, i.e.,

$$\left(\frac{C_p}{N_0}\right)N\,\frac{dT}{dt} + \left(\frac{C_p}{N_0}\right)T\,\frac{dN}{dt} = \left(\frac{C_p}{N_0}\right)T_\infty\,\frac{dN'}{dt} + \sum_i D_i \left.\frac{dN_i}{dt}\right|_{\text{chemistry}} \tag{3}$$

Here, N_0 is Avogadro's number, C_p the molar specific heat at constant pressure, dN'/dt the rate of ingestion of ambient particles, T_∞ the ambient temperature, and D_i the ith specie dissociation energy. Assuming with Sutton that $dN/dt = dN'/dt$ (i.e., neglecting particle number change due to chemical reaction) and introducing the ideal gas law, from which we obtain

$$kT(dN/dt) = P(dV/dt) - Nk(dT/dt) \tag{4}$$

we see that Eq. (3) takes the form

$$\frac{1}{T}\,\frac{dT}{dt} = \frac{2}{3}\left(1 - \frac{T(t)}{T_\infty}\right)t^{-1} + \frac{1}{T_\infty}\sum_i \left(\frac{D_iN_0}{C_p}\right)\frac{1}{N(t)}\left.\frac{dN_i}{dt}\right|_{\text{chemistry}} \tag{5}$$

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[Ref. 3, Eq. (17), correcting typographical errors]. Substituting this result into Eq. (2) we obtain

$$\left.\frac{dn_i}{dt}\right|_{\text{mixing}} = \frac{2}{3}\,[n_i(\infty) - n_i(t)]t^{-1} - \frac{n_i(\infty)}{T(t)} \sum_j \left(\frac{D_j N_0}{C_p}\right) \frac{1}{N(t)} \left.\frac{dN_j}{dt}\right|_{\text{chemistry}} \tag{6}$$

Comparison of Eqs. (1) and (6) shows that the mixing rate employed in Sutton's model,[2] Eq. (6), will differ from that of Lin and Hayes,[4] Eq. (1), unless the last term on the RHS of Eq. (6), arising from the rate of change of enthalpy due to chemical reaction, is negligible.

If the change of enthalpy due to chemical reaction is negligible and neglect of the last term on the RHS of Eq. (5) is a good approximation the temperature can be obtained analytically by direct integration in the form

$$T(t) = T_\infty/[1 - (1 - T_\infty/T_0)(t_0/t)^{2/3}] \tag{7}$$

with t_0 and T_0 the time and temperature at breakthrough, respectively. Taking, $t_0 \cong 1 \times 10^{-3}$ sec, $T_0 \cong 600°\text{K}$, with $T_\infty \cong 300°\text{K}$, we find that Eq. (7) is, in fact, in good agreement with Sutton's 40 Torr result for the wake temperature history (Ref. 2, Fig. 4). It is not quite clear, however, that the last term on the RHS of Eq. (6) will also be negligible if the related term on the RHS of Eq. (5) is negligible. Therefore, the mixing rate of Eq. (6) may differ from that of Eq. (1) even if Eq. (7) is a good approximation to the wake temperature history. Certainly for those parts of turbulent wakes in which the rate of change of enthalpy due to chemical reactions is not negligible, the mixing rate of Eq. (6) will differ from that of Eq. (1). Further, for those wake regions in which $dN/dt = dN'/dt$ [see Eq. (3)] is a poor approximation (i.e., the rate of change of wake particles due to chemical reaction is not negligible) the entire procedure of Eqs. (3), (5), and (6), is invalid. In such a case, a temperature history consistent with the assumptions of the homogeneous mixing model of Lin and Hayes,[4] Eq. (1), can be obtained from Eq. (4) by setting

$$\frac{dN}{dt} = n(\infty)\,\frac{dV}{dt} + \sum_i \left.\frac{dN_i}{dt}\right|_{\text{chemistry}} \tag{8}$$

with the rates of change of specie numbers due to chemistry, dN_i/dt, obtained from the chemical reaction rate equations. Alternately, following the original work of Lin and Hayes,[4] the correct mixing rate and conservation equations [Ref. 4, Eqs. (4–7)] can be used, although a slight pressure mismatch over ambient in the far wake apparently occurs following this procedure (Ref. 4, p. 1219).

Discussion

Although the homogeneous mixing model can be formulated completely consistently in the far wake making use of Eqs. (1, 4, and 8), we note that the assumption of an infinite viscous dissipation rate, with accompanying infinite microscopic molecular mixing rate, would seem to be in disagreement with the observation of persistent large scale turbulent eddys in the far wake,[11] where thermal conduction and molecular diffusion should dominate temperature decay and mixing rates, respectively.[12] Further, homogeneous molecular mixing is apparently incompatible with recent interpretation[13] of measured wake radiation[14] and a qualifying assertion[2] that computed wake chemistry is insensitive to the details of the molecular mixing model employed would seem to be in disagreement with previous investigations.[7–9]

Nevertheless, the computations of Sutton[2] utilizing homogeneous mixing have apparently resulted in predicted electron line-density decay rates in excellent agreement with experiment.[1] We note here, however, an apparent numerical inconsistency in the computations which may be related to the considerations of the preceding section. Specifically, in Ref. 2 the electron line density of Fig. 3 (40 Torr case) should be simply related to the fractional electron concentration, χ_e, of Fig. 4; however, the fractional electron concentration obtained from the equation

$$\chi_e = n_e/n(t) = (N_e/l)/[n(t)A] \tag{9}$$

is in disagreement in the interval $4 \times 10^{-3}\ \text{sec} \leq t \leq 8 \times 10^{-3}$ sec by as much as two orders-of-magnitude with the results of Fig. 4, Ref. 2. In Eq. (9) the electron line density, N_e/l, is obtained from Fig. 3 of Ref. 2, the wake cross-sectional area, A, is obtained from the radius expression of Eq. (1), Ref. 4, and the total wake number density, $n(t)$, is obtained from the ideal gas law and temperature history of Eq. (7). In view of the agreement of Sutton's predicted temperature history with Eq. (7) the possible internal inconsistency of his procedure may not arise in the 40 Torr case of interest here, unless the chemical enthalpy term on the RHS of Eq. (6) is not negligible. An alternate source of the discrepancy perhaps may be found in the fact that Sutton's computations predict a near steady-state electron attachment-detachment cycle in the far wake, introducing the numerical difficulties associated with integrating rate equations containing the difference of two large almost equal terms [See Ref. 2, Eqs. (12) and (13)].

We suggest that a careful examination of the assumptions underlying the various mixing models employed in wake chemistry calculations, and of the computational procedures involved therein, would be most desirable, especially in view of a continuing program of electron line-density decay measurements, proposed mass spectrometer experiments, and other related investigations, at this and other laboratories.[15]

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