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NOTE ON IGNITION BY A HOT CATALYTIC SURFACE*

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In a previous paper [1], we applied asymptotic methods based on large values of the nondimensional activation temperature to study ignition of a reactive material, semi-infinite in extent, subjected to a step increase in temperature at its planar surface. In appendices of that paper, the analysis was extended to consider effects of reactant consumption and of surface catalysis, the latter involving catalytic removal of fuel by the surface at which the temperature increase is imposed. There appears to be increasing interest in this last problem, in connection with situations in which reactants are exposed to hot surfaces which possess the capability of consuming fuel. Therefore, additional considerations, reported herein, have been pursued.

A generalization of the formulations in [1, Appendices A and B] may be introduced by assigning to the hot surface a finite, nonzero rate for the catalytic consumption of fuel. The equations to be solved are [1, (A1) and (A2)], with the last boundary condition, $(\partial Y/\partial\xi)_{\xi=0}=0$, replaced by

$$\left(\frac{\partial Y}{\partial \xi}\right)_{\xi=0} = -k_s(1-Y_s), \tag{1}$$

where $(1-Y_s)$ denotes the reactant concentration divided by its initial value. Here k_s is a reaction-rate constant for surface catalysis and is assumed to be independent of Y_s. The boundary condition in Appendix A corresponds to the limit as $k_s \to 0$, and that in Appendix B is $Y_s = 1$, which corresponds to the limit as $k_s \to \infty$. It may be noted that by replacing ξ by $\int_0^{\xi}(\rho/\rho_\infty)\,d\xi$, where ρ denotes the density of the reactive medium, the analysis can be made to apply to gaseous reactants.

The analysis of Appendix A can be generalized without difficulty to deal with the distinguished limiting case in which both C and $K = k_s/\sqrt{L}$ are of order unity. Here, L is the Lewis number and $C=[\rho c(T_s-T_i)/q]\sqrt{L/\pi}$, where c denotes the heat capacity of the reacting medium, T_s the surface temperature, T_i the initial temperature, and q the heat released per unit mass of reactant consumed. The parameters C and K measure the effects of reactant consumption homogeneously and at the surface, respectively. It is then found that (A15) is replaced by

$$Y_s(\tau)=\frac{1}{\sqrt{\pi}}\int_0^{\tau}\left\{C\left[\frac{1}{\sqrt{\tau'}}-\sqrt{Y_s(\tau')+\frac{1}{\tau'}-1}\right]+K[1-Y_s(\tau')]\right\}\frac{d\tau'}{\sqrt{\tau-\tau'}}, \tag{2}$$

as the integral equation describing the evolution with time of the surface product concentration Y_s, in the first approximation. Here, the first term in the integral accounts for the effect of the homogeneous reaction, while the second takes into account the effect of the surface reaction.

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The nondimensional ignition time τ_I is now a function of C and K. For small values of C and K of order unity, Y_s is given in a first approximation by the solution to (2) for $C = 0$, namely

$$Y_s = 1 - e^{K^2\tau} \operatorname{erfc}(K\sqrt{\tau}). \tag{3}$$

The ignition time in the first approximation then is the time at which the square-root term in (2) becomes imaginary, i.e.,

$$\tau_I = \frac{e^{-K^2\tau_I}}{\operatorname{erfc}(K\sqrt{\tau_I})}. \tag{4}$$

Solution of this transcendental equation provides τ_I as a function of K for small values of C. In particular, as $K \to 0$ it is found that $\tau_I \to 1$, in agreement with the first approximation obtained in the main text in [1].

If $K \gg 1$, then ignition will not occur before Y_s reaches a value near unity, and the analysis of Appendix B becomes the appropriate means for calculating τ_I. Yu Pen Su has brought to our attention the fact that we inadvertently interposed ε and $1/\varepsilon$ in the definitions leading to the final formulas in Appendix B. Here ε is the small parameter, inversely proportional to the overall energy of activation. Beginning with (B2), the previous text should read as follows:

$$\frac{\partial^2\psi}{\partial z^2} = -\sigma(z - B\psi)\, e^{\psi - z}, \tag{B2}$$

where $z = \xi/\varepsilon\sqrt{\pi\tau}$, $\sigma = \varepsilon D\tau\sqrt{L}/2$, and $B = \gamma\sqrt{L}/\varepsilon$. The boundary and matching conditions in the first approximation require $\psi = 0$ at $z = 0$ and $\partial\psi/\partial z = 0$ at $z = \infty$. Note that the scaling results in reactant consumption being significant for γ of order ε (B of order unity), just as in the noncatalytic problem of Appendix A with L of order unity.

The final paragraph of [1] is unchanged, except for replacing $\tau_{ig} = \varepsilon/\sqrt{L}$ by $\tau_{ig} = (\varepsilon\sqrt{L})^{-1}$ in the last line. The revised estimate for the ignition time, $\tau_I = (\varepsilon\sqrt{L})^{-1}$, when compared with the result $\tau_I = O(1)$ for a noncatalytic surface, is consistent with the known fact that through removal of reactant from the reaction zone, catalysis tends to lengthen the ignition time. Improved accuracy may be obtained by developing the analysis of Appendix B to calculate $\sigma_I = \varepsilon\tau_I\sqrt{L}/2$ as a function of $B = C\sqrt{\pi}$.

This development entails solving (B2) subject to $\psi(0) = \psi_z(\infty) = 0$ and obtaining ψ_∞ as a function of σ and B, where the subscript ∞ identifies $z = \infty$. This equation has a unique solution for all positive values of σ if $B > 1$; the resulting value ψ_∞ increases monotonically with σ for all values of $B \geqq 1$, as shown in Fig. 1. For $B = 1$, there is only one solution for $\sigma < \sigma_I = \frac{1}{2}$. If $B < 1$, then there are two solutions for ψ_∞ for all values of $\sigma < \sigma_I(B) < \frac{1}{2}$ and no solution for $\sigma > \sigma_I(B)$; the solution with the larger value of ψ_∞ is not attainable physically. For the solution with the smaller value of ψ_∞, the value of ψ_∞ increases with increasing σ; when σ approaches $\sigma_I(B)$, a time-derivative term should be included in (B2), and extending the solution to larger σ would show the development and propagation of a premixed flame. The value $\sigma_I(B)$ provides a first approximation to the ignition time if $B \leqq 1$.

It is interesting to note that when (B2) is written in terms of the "concentration" variable $z/B - \psi$ and the distance variable $z/B + (1-B)^{-1} \ln(2\sigma B^3)$, it reduces to the equation describing the reaction-zone structure in the premixed-flame regime of [2], although the boundary conditions are different. When $B \gg 1$ and $\sigma \gg 1$, an analysis

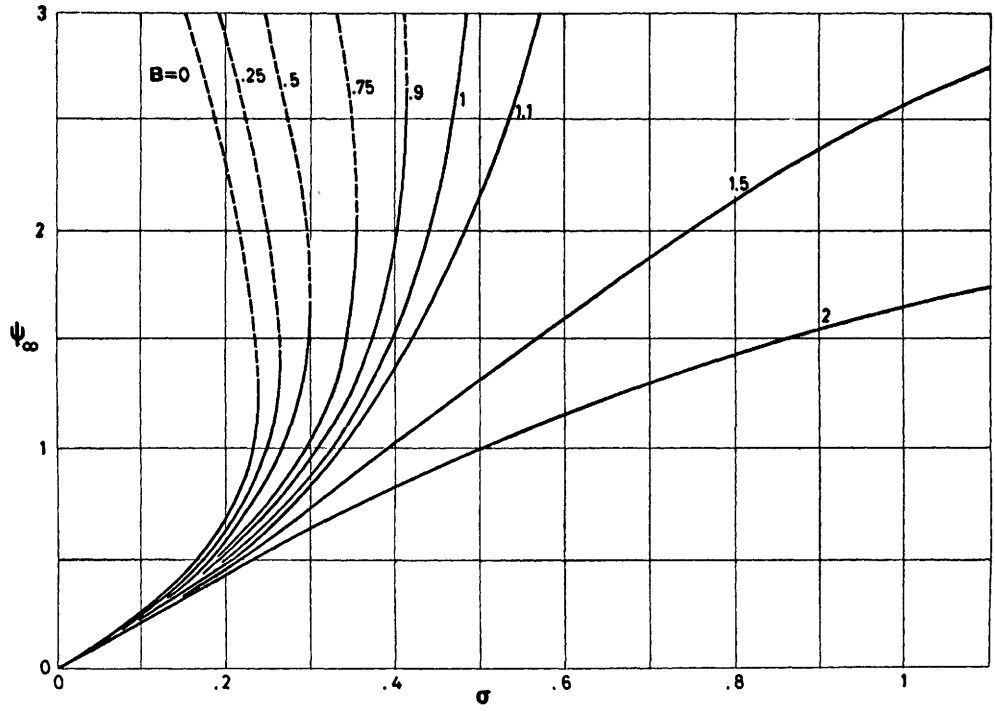

FIG. 1. *The dependence of the temperature increment at $z = \infty$ on the nondimensional time σ for various values of the reactant consumption parameter B, as obtained from a numerical integration of* (B2).

identical to that of [2, § 5] can be used to obtain the solution to (B2). It can be shown that a premixed flame has then been established, separating a region of equilibrium close to the wall, where $z/B - \psi = 0$, from an outer region of frozen flow. The temperature in the equilibrium zone decreases linearly from the wall to the flame, while it would increase for $B < 1$. The resulting solution for ψ_∞ when $B > 1$ and $\sigma \gg 1$ is

$$\psi_\infty = (1-B)^{-1} \ln \left\{ \frac{[1 - 1.344(1-B) + 0.6307(1-B)^2]}{2\sigma B^3} \right\}. \tag{5}$$

For $B > 1$, the heat release is so small in comparison with the energy associated with the temperature increase at the surface, that with strong catalysis the reactant consumption is sufficiently great to prevent a singular event identifiable with ignition from occurring, and the process is calculated to evolve continuously with time. Nevertheless, to the extent that a time to ignition can be defined, $\tau_I = (\varepsilon\sqrt{L})^{-1}/B^3$ provides an estimate of that time.

For $B \leqq 1$, a table of $\sigma_I(B)$, with $\sigma_I = \varepsilon\tau_I\sqrt{L}/2$, is as follows:

B	0.00	0.25	0.50	0.75	0.90	1.00
σ_I	0.239	0.265	0.300	0.357	0.417	0.500

It is not easy to calculate $\sigma_I(B)$ for small values of $1 - B$, but of course, σ_I varies over a relatively small range in this region.

We wish to thank M. Rodriguez for carrying out the numerical analysis of (B2), leading to Fig. 1 and the table.

These results show that for $K \gg 1$, at a given value of C the ignition time τ_I depends on $\varepsilon\sqrt{L}$ but is independent of K in a first approximation. On the other hand, (2) indicates that if K is not very large, then when C is given, τ_I depends on K but is independent of $\varepsilon\sqrt{L}$ in the dominant order. The dependence of τ_I on $\sqrt{\pi}\,C$ for various values of K as implied by (2) is illustrated in Fig. 2. In this figure, the values at $B = 0$ are given by (4). The curves shown for $K = 2$ and for $K = 3$ are obtained from an analysis of (2) for K large and for B of order unity; this analysis, outlined below, is accurate within a few percent for these values of K. The same analysis was employed to plot an approximate curve for $K = 1$, with arbitrary corrections approaching 25% introduced near $B = 0$ to achieve agreement with (4). The curve shown for $K = 0$ represents an improvement over [1, Fig. 3]. The numerical integration employed to obtain [1, Fig. 3] is difficult for $C \gtrsim 0.5$, and consequently suffered significant inaccuracies. In particular, the reported value of 0.89 for the limit of C as $\tau_I \to \infty$ is in error; it will be reasoned below that this limit is $C = 1/\sqrt{\pi} \approx 0.56$ and is consistent with the ignition time approaching infinity at $B = 1$ for all values of K, as indicated in Fig. 2.

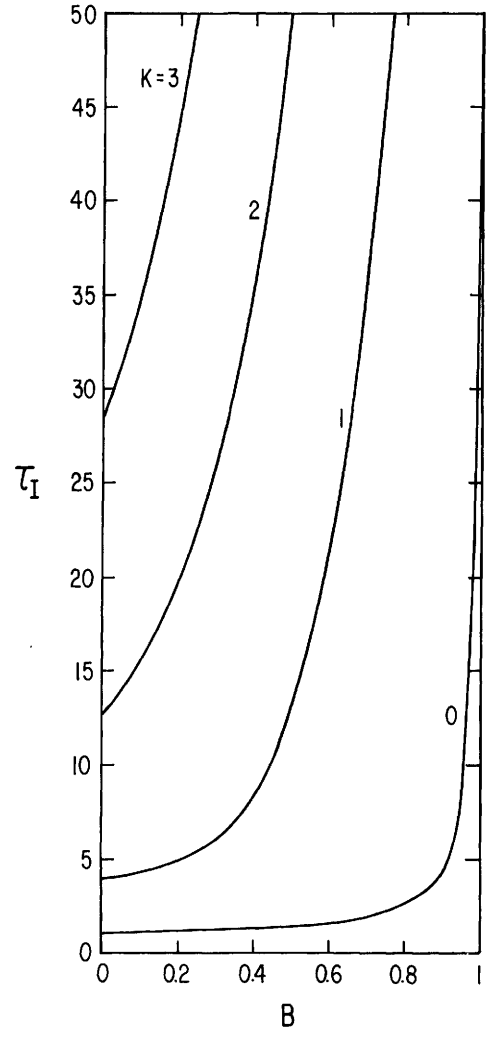

FIG. 2. *The dependence of the nondimensional ignition time on the reactant consumption parameter for various values of the surface catalyticity parameter.*

For $K=0$ and large τ, put $\tau'=u\tau$ and $Y=1-y$, and consider $y\ll 1$ and u of order unity. Then (2) may be seen to be consistent with $y=a/\tau$ for large τ, where a is a constant. Substitution into (2) results in $1-\sqrt{1-a}=1/B$, which is acceptable only if $B>1$. For smaller values of B, $(Y-1+1/\tau)^{1/2}$ in (2) becomes imaginary at a finite value of τ that corresponds to τ_I. This same reasoning may be extended to $K\neq 0$; the same results are obtained for $B>1$, although there is a divergence in the K term for small u that requires special consideration. Since it has been indicated in [1, Appendix A] that for $K=0$, $\tau_I=1+(1-2/\pi)B+\cdots$ for small values of B, the approximation

$$\tau_I=(1-2B/\pi)(1-B)^{-1} \tag{6}$$

seems reasonable for $K=0$. This formula, which has been employed in Fig. 2, possesses the correct value and slope at $B=0$ and the correct asymptote as $\tau_I\to\infty$, but an improved numerical integration is needed to evaluate its accuracy properly.

For large K and B of order unity there are two stages in (2), an early stage in which τK^2 is of order unity and a late stage in which τ/K^2 is of order unity. In the early stage with $v=\tau K^2$, the expansion $Y=Y_0(v)+K^{-2}Y_1(v)+\cdots$ may be introduced and the results $Y_0=e^v\,\mathrm{erfc}\,(\sqrt{v})$ and

$$Y_1=\frac{1}{2\pi}\int_0^v \frac{B[1-Y_0(v')]\sqrt{v'}-2\sqrt{\pi}\,Y_1(v')}{\sqrt{v-v'}}\,dv'$$

derived. For large v, these yield $Y_0=1-(\pi v)^{-1/2}$ and $Y_1=B/2\pi$, which demonstrate the need for the late stage when substituted into (2). In the late stage with $w=\tau/K^2$ and $y=K^2(1-Y)$, (2) becomes

$$\frac{1}{\pi}\int_0^w \left\{B\left[\frac{1}{\sqrt{w'}}-\sqrt{\frac{1}{w'}-y(w')}\right]+\sqrt{\pi}\,y(w')\right\}\frac{dw'}{\sqrt{w-w'}}=1-\frac{y}{K^2}.$$

With the term y/K^2 neglected for large K, this integral equation can be solved to yield

$$B\left(\frac{1}{\sqrt{w}}-\sqrt{\frac{1}{w}-y}\right)+\sqrt{\pi}\,y=\frac{1}{\sqrt{w}}, \tag{7}$$

which provides $y(w,B)$ for w of order unity. For small w this gives $y\approx(\pi w)^{-1/2}$, which matches with the early stage. For large w, (7) yields $y=b/w$ with $1-\sqrt{1-b}=1/B$ if $B>1$. If $B<1$, then there is an ignition time w_I such that $y=1/w_I$ at $w=w_I$, and consequently (7) indicates that $B/\sqrt{w_I}+\sqrt{\pi}/w_I=1/\sqrt{w_I}$. In the original variables this formula is $\tau_I=\pi K^2(1-B)^{-2}$, which has been used in the curves for $K\neq 0$ in Fig. 2.

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