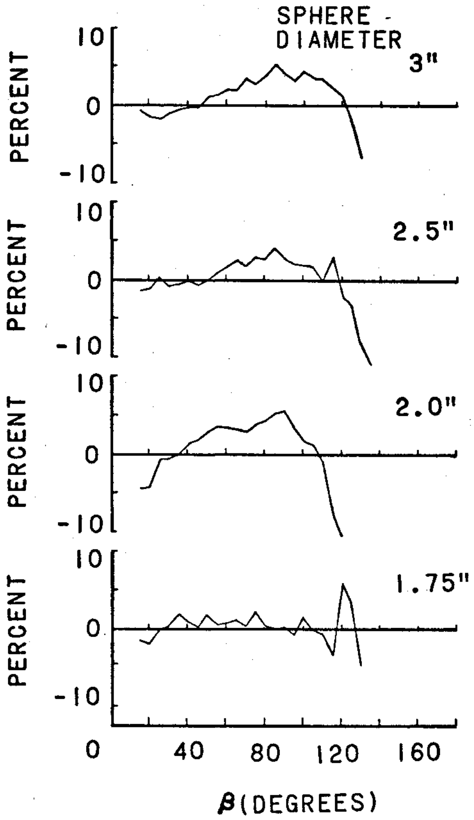

Fig. 3 Percent deviation between the theoretical values and experimental data as a function of β for the Lambert analysis.

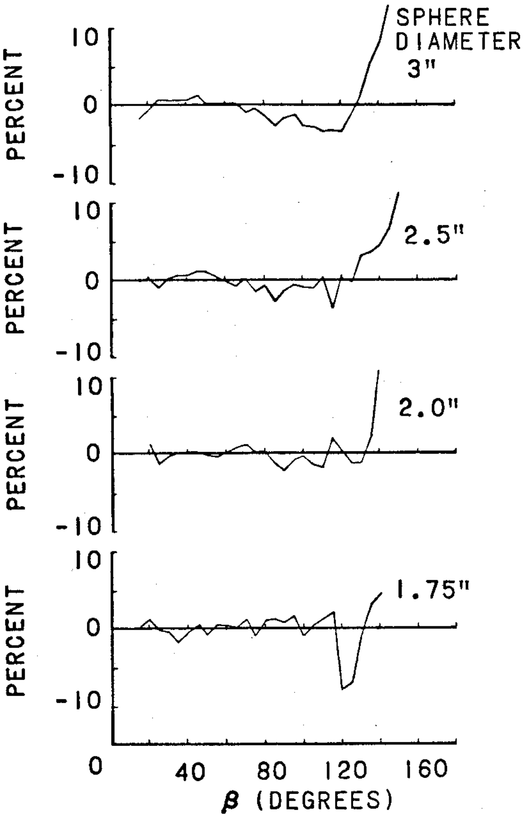

Fig. 4 Percent deviation between the theoretical values and experimental data as a function of β for the s factor analysis.

Conclusions

The reflectance models of Lommel-Seeliger and Euler do not accurately describe the power distribution upon reflection from the spheres. That is, the percentage deviation varies in a nonrandom fashion, thus the shape of the curves do not approximate the shape of the data.

The results do indicate that the classical Lambert analysis is a fair approximate model. But, because the theoretical values do deviate from the data (especially for the large spheres), it must be concluded that the Lambert curve shape does not fit the data curve exactly. However, the fit would probably be accurate enough for most engineering applications.

The s factor analysis does produce an adequate approximate model. The percentage deviation of the theoretical values and the data is less than 3%. The nonrandom deviation, however slight, indicates the s factor analysis cannot be said to describe the shape of the data exactly. However, the fit is well within the accuracy needed for engineering application.

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Some Comments on the Dirac-Delta Approximations for Chemical Reactions

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Nomenclature

A = preexponential factor
C = coordinate compensation factor
c_p = specific heat
D = binary diffusion coefficient
$D_{III,g}$ = third Damköhler number
d = diameter
E = first exponential integral
E_g = activation energy for gas phase oxidation
I,I' = integral, Eqs. (3) and (4)
$\dot{m}$ = gasification rate
n = overall order of reaction
n_i = order of reaction with respect to species i
p = pressure
Q = heat of gasification
R = gas constant
r = radius
T = temperature
W = molecular weight
Y = mass fraction
ϵ = flux fraction
ξ = dimensionless burning rate, $\dot{m}/4\pi\rho Dr$
η = arbitrary coordinate
θ = dimensionless temperature
θ_1,θ_2 = Eqs. (2b)

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υ = stoichiometric coefficient
ρ = density

Subscripts

g = gas phase
O = oxygen
p = peak burning
V = vapor or pyrolysate gas
w = wall or surface
∞ = ambient, infinity

Superscript

$()^*$ = stoichiometric surface or maximum temperature region

I. Introduction

MANY analytical problems, either in premixed or in diffusion flames, are nonlinear because of the exponential function in the constitutive chemical rate equations. Hence, such rate equations often are approximated. One of the recent approximations is the introduction of the Dirac-delta function, both in laminar and turbulent flames. A literature survey reveals that the Dirac-delta approximations are being introduced in arbitrary coordinates. As such the qualitative results could differ, depending on the coordinate in which such approximations are introduced. However, the physical quantity must remain invariant.

A rational procedure is developed mathematically, and with the introduction of a coordinate compensation factor, a link is established between the invariant physical or conserved quantity and the quantity obtained from Dirac-delta approximations introduced in arbitrary coordinates. This procedure first is checked with previous results for a premixed laminary flame. The method is then repeated for diffusive burning of a char particle undergoing two step oxidation processes with finite chemical kinetics control. The qualitative results thus obtained are found to be in good agreement with the numerical results obtained without the Dirac-delta approximations, thus validating the present analysis.

Unlike the diffusion-controlled burning regimes, the ignition and extinction phenomena are strongly dependent upon the interbalance of the finite chemical heat generation and the heat loss from the reaction zone. Mostly because of the exponential behavior of the chemical reaction rate, the problems either in premixed or diffusion flames are nonlinear. Consequently, in order to achieve simplified solutions, the constitutive chemical reaction rate equations are approximated. Such approximations are the Spalding's power polynomial fit in terms of temperature[1] for the estimation of flammability limits (premixed flame) and the Dirac-delta approximation introduced by Peskin[2] for the ignition of droplets (diffusion flame). Later Marathe and Jain[3] applied the Dirac-delta technique to the problem of flame characteristics of an opposed jet diffusion flame. A similar approximation is used for the anlaysis of ignition and combustion of coal/carbon particles.[4,5]

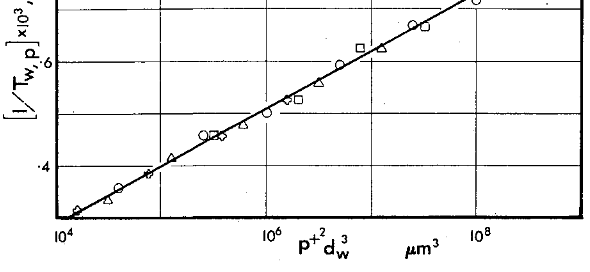

Fig. 1 Peak burning temperatures vs $p^{+2}d_w^3$; —— approximate theory; numerical results: □ 200 μm, ○ 100 μm, △ 50 μm, ⌖ 25 μm; $1/T_{w,p} = -0.151425\times10^{-3} + 0.109985\times10^{-3}\log d_w^3 p^{+2}$; slope (fit) = 0.10999×10^{-3}, slope (theory): 0.105×10^{-3}.

Approximations of the chemical reaction at a surface find increasing use in recent turbulent combustion models.[6] However, based on the mathematical definition, the Dirac-delta function is dimensional (in a mathematical sense), and as such, the magnitude of the integral varies by a factor depending on the coordinate system. Hence, the quantitative analysis of the results could be different depending upon the coordinate in which the Dirac-delta approximation is used. On the other hand, the physical quantity (either total species consumed or heat generated) must remain invariant to the coordinate transformation. The present technical note provides a link between the invariant physically meaningful quantity and the quantity obtained from the Dirac-delta approximations introduced in an arbitrary coordinate.

II. Problems and Solutions

As an example, the problem of a coal particle under pyrolysis or of a droplet evaporating into the hot stagnant atmosphere may be considered. The gases evolving from the surface oxidize in the gas phase. The diffusive flux fraction of oxygen necessary for the finite chemical reaction rate is given as

$$\epsilon_O = -\left(\frac{D_{III,g}\xi_w^2}{\xi^4}\right)\int_O^{\xi_w} Y_O^{n_O}\, Y_V^{n_V}\left(\frac{e^{-1/\theta}}{\theta^n}\right)d\xi \tag{1}$$

For a reaction with a high activation energy, the maximum reaction rate occurs when the fuel and oxidizer concentrations are in stoichiometric proportion.[7] Thus,

$$\epsilon_O = -\frac{D_{III,g}\xi_w^2\,(Y_O^*)^{n_O}\,(Y_V^*)^{n_V}}{(\xi^*)^4\,(\theta^*)^n\,(d\theta/d\xi)^*}\int_{\theta_2}^{\theta_1} e^{-1/\theta}d\theta \tag{2a}$$

where

$$\theta_1 = \theta^* - \quad \text{and } \theta_2 = \theta^* \tag{2b}$$

Note that a transformation from ξ to θ coordinate was carried out. The term $(d\theta/d\xi)^*$ must be evaluated near the region of stoichiometry, and it is a mean value of the gradients for the burnt and unburnt regimes. Thus, 1) for the flow of a combustible mixture through a tube (e.g., the problem in Ref. 1.), the gradient is evaluated as the mean of gradients of the unburnt and burnt sides (such a procedure checks with Spalding's results for the heat liberation at the time of extinction); 2) for the surface oxidation of carbon monoxide gas, generated by oxidation of a carbon particle, the thermal gradient is evaluated on the gas side[4]; and 3) for the oxidation of vapor from a droplet or pyrolysate gases from a coal particle, the thermal gradient is evaluated as the mean value around the stoichiometric surface.[4]

In Eq. (2), the integral is evaluated as follows

$$I' = \int_{\theta_2}^{\theta_1} e^{-1/\theta}d\theta = \theta_1 e^{-1/\theta} - \theta_2 e^{-1/\theta_2} + E_1(\theta_2) - E_1(\theta_1) \tag{3}$$

Then

$$\epsilon_O = -\frac{D_{III,g}\xi_w^2\,(Y_O^*)^{n_O}\,(Y_V^*)^{n_V}e^{-1/\theta^*}I}{(\xi^*)^4\,(\theta^*)^n\,(d\theta/d\xi)^*} \tag{4a}$$

where

$$I = I' e^{1/\theta^*} \tag{4b}$$

If one introduces the Dirac-delta approximation for Eq. (1), the result is

$$\epsilon_O = -\frac{D_{III,g}\xi_w^2\,(Y_O^*)^{n_O}\,(Y_V^*)^{n_V}e^{-1/\theta}C}{(\xi^*)^4\,(\theta^*)^n} \tag{5}$$

where C is the coordinate compensation factor. Comparison of Eqs. (5) and (4) shows that, for the case of ignition or burning of coal particles or droplets under finite chemical kinetics,

$$C=I/(d\theta/d\xi)^* \tag{6a}$$

More generally, if η is an arbitrary coordinate in which the Dirac-delta approximation is introduced, then

$$C=I/(d\theta/d\eta)^* \tag{6b}$$

Using polynomial and rational approximations for the first exponential integrals[8] and for the high-activation energy of the reaction,

$$C=\theta^*/(d\theta/d\xi)^* \tag{7}$$

Then if ξ is the coordinate other than θ, the factor C will depend on the gradient $(d\theta/d\xi)^*$. According to previous literature,[2,3] the coordinate compensation factor will be unity for any coordinate in which the Dirac-delta approximation is introduced, whereas the present analysis shows a dependence of the factor on the thermal gradient, which consequently serves to maintain the invariance of the physical quantity. Thus, for the ignition of a droplet or a volatile coal particle, where $\theta_w<<\theta_\infty$ and $\theta^*=\theta_\infty$ under adiabatic ignition conditions,

$$C=2\theta_\infty/[Q_w/(E_g/R)c_p] \tag{8}$$

whereas for a heated carbon particle burning in cold surroundings, where $\theta_w>>\theta_\infty$ and $\theta^*=\theta_w$,

$$C=\theta_w(e^{\xi_w}-1)/(\theta_w-\theta_\infty)\simeq\xi_w \quad \text{for } \xi_w<<1 \tag{9}$$

III. Results

A numerical solution for the burning rate of a heated carbon particle in cold surroundings was carried out.[9] The chemical kinetics of the process was considered to be a finite two-step oxidation process in which C oxidizes to CO on the particle surface and CO oxidizes to CO_2 in the gas phase. The solution revealed a maximum in the burning rate at a particular particle temperature. Then the variation of this particle temperature with respect to the particle size and ambient pressure was studied. In order to establish a correlation of the results in terms of the particle size and ambient pressure with a single dimensionless group, a Dirac-delta approximation was introduced following the argument introduced in the present technical note. The results of the calculations for the variation of the temperature at the peak burning rate with the particle size and ambient pressure are presented in Fig. 1. The solid line presents results from the approximate theory and the symbols the numerical calculations. The agreement between the two is excellent.

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Condensed Phase Heat of Reactions of Phenol-Formaldehyde Composite Propellants

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Introduction

THERE exists sufficient evidence[1,2] to indicate the possibility of some exothermic solid-state reactions in composite propellants. Thus, as in the case of double base propellants, the energy necessary to heat the composite propellant surface is supplied in part by these exothermic reactions and in part by energy transferred from the hotter flame zone. Since most jet propulsion devices operate at comparatively low pressure where only a small amount of energy returns from the flame, these exothermic reactions occurring in the condensed phase are of practical importance.

Recently Kirby and Suh[3] have reported that there exists no reliable method of direct measurement of the condensed phase heat of reactions of solid propellants. However, they suggested an indirect method of computation based on the theory of Adams[4] and experimental technique of Suh et al.[5] The same has been adopted in this communication.

Experimental

For a solid undergoing several consecutive reaction steps to give gaseous products where the first of these is an exothermic zero-order reaction, Adams[4] has shown that heat Q for this initial reaction is

$$Q=\bar{C}_p\ (T_s'-T_o) \tag{1}$$

where $\bar{C}_p$ and T_o are the average specific heat and initial temperature of the propellants respectively. T_s' is the minimum surface temperature at the solid surface with no heat feedback from the gas phase. His analysis further predicted that at T_s' the propellant should burn at a rate approaching infinity.

Recently Girdhar et al.[5] have studied the effect of initial temperature on burning rates of composite propellants by making the measurements in an air thermostat maintained at the desired initial temperature. The experimental data were found to fit the relation[6]

$$r=Cp^n/(T_s-T_o) \tag{2}$$

The surface temperature, T_s was calculated from the slope and intercept of the plot of $1/r$ vs T_o. It can be seen from Eq.

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