Effects of Thermal Radiation on the Acoustic Response of Solid Propellants

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Theoretical calculations are given for the propellant response function when thermal radiation of the burnt gases is taken into account. Under the assumption that the gas radiates as a gray body, it is found that radiation effects may significantly alter the response function at low frequencies for the low propellant burning rates that are commonly found at low pressures. Thus, this mechanism may offer a partial explanation of the fact that experimental values for the response function at low frequencies and low burning rates tend to be larger than is expected from existing theories. The method of calculation is based on a second-order perturbation scheme where the perturbation parameter is a measure of the ratio of transfer by radiation to convective energy transfer.

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Nomenclature
                                                                                           S
                                                                                                     = entropy
                                                                                                     = reciprocal length associated with steady-state
             = (\bar{P}/\bar{m})(\partial \bar{m}/\partial \bar{P})\bar{G}_0; see Eqs. (3a) and (A1b)
                                                                                                           radiative fluxes and temperature [defined in Eq.
             = (1/\bar{m})(\partial \bar{m}/\partial \bar{G}_0)\bar{P}; see Eqs. (3a) and (A1c)
             = no-flow sound speed (\gamma \bar{P}/\bar{\rho})^{1/2}
                                                                                                     = reciprocal length obtained from dispersion equation
                constant pressure heat capacity
                                                                                                           for a time-dependent radiating gas [see Eq.
                heat capacity of the solid propellant
                                                                                                           (11d)
             = constant volume heat capacity
                                                                                                     = time
    C_2, C_3 = coefficients defined in Eq. (10b)
                                                                                                        temperature
                [C_s(\overline{T}_0 - T_c)/(C_p\overline{T}_0 + h)][(\Lambda - 1)/\Lambda]; see Eq. (2c) (C_s/C_p)(\Lambda - 1); see Eq. (2c)
                                                                                                        velocity
\stackrel{\widetilde{E}_2}{f}_{F_M}
                                                                                                        coordinate measuring distance from propellant sur-
                frequency
             = \bar{m}(\partial \bar{q}_0/\partial \bar{m})\bar{r}_b; see Eq. (A3a)
                                                                                          X
                                                                                                     = (\beta \mathfrak{F} + \alpha C_p T_0)/\beta \mathfrak{F} = 1 + \alpha C_p T_0/\beta \mathfrak{F}
F_T
                T_b(\partial \bar{q}_0/\partial \bar{T}_b)_{\bar{m}}; see Eq. (A3a)
                                                                                                     = dimensionless distance or optical depth, \int_0^x \bar{k} dx
                                                                                          z
                temperature gradient (\partial T/\partial x)
                                                                                                         [(\lambda \tilde{G}_0 + \bar{q}_0)/\bar{m}] [\partial \bar{m}/\partial (\lambda \tilde{G}_0 + \bar{q}_0)] \bar{\tau}_0; \text{ see Eq. (2d)}   (\bar{T}_0/\bar{m})(\partial \bar{m}/\partial \bar{T}_0)(\lambda \bar{G}_0 + \bar{q}_0); \text{ see Eq. (2d)} 
                enthalpy per unit mass (including enthalpy of reac-
                                                                                           β
\Delta H_v(T)
             = enthalpy difference for change of phase (solid to
                                                                                                        ratio of specific heats
                    gas) at temperature T (positive for endothermic
                                                                                                        (\sigma_* \bar{T}_b^4/\bar{m}C_p\bar{T}_b)
                    reaction)
                                                                                                        see Eq. (11e)
                                                                                           \Delta_{\nu}
             = h_v - C_s T_c
h
                                                                                                        dimensionless pressure erturbation; P = \bar{P}(1 + \epsilon)
             = \Delta H_v(T_c) - (C_p - C_s)T_c
= h + C_p\overline{T}_0
                                                                                                     = (\bar{T}_f - \bar{T}_b)/\bar{T}_b
                                                                                           Č
                                                                                                     = dimensionless entropy perturbation; S = \bar{S} + C_p \theta
             = positively and negatively directed radiative heat
                                                                                          λ
                                                                                                     = heat conductivity
                                                                                                        (\frac{1}{2})[1 + (1 + 4i\omega\tau_s)^{1/2}]
                    fluxes
             = dimensionless perturbed radiative heat fluxes;
                                                                                                        dimensionless perturbed mass flux; m = \bar{m}(1 + \mu)
                    I^+ = \bar{I}^+ (1 + \hat{s}^+), etc.
                                                                                                        frequency dependent functions; see Eqs. (17b) and
                                                                                           \xi_1, \; \xi_2
             = conditioning temperature sensitivity index for steady-state burning, (T_c/\bar{m})(\partial \bar{m}/\partial T_c)\bar{P}
                                                                                                        (17c) density
                                                                                                        dimensionless perturbed density; \rho = \bar{\rho}(1+\sigma)
Stefan-Boltzmann const \approx 1.37 \times 10^{-12} cal/cm<sup>2</sup>-sec
             = frequency dependent function for a radiating gas
                    analogous to the constant j for a nonradiating
                                                                                                           (°K)4
                    gas [see Eqs. (20a) and (20c)]
                                                                                                         characteristic time associated with heat conduction in
             = quantity defined in Eq. (19d)
                                                                                                           solid (\lambda_s \rho_s/\bar{m}^2 C_s)
             = radiation absorption coefficient
                                                                                                         dimensionless perturbed temperature; T = \overline{T}(1 +
                                                                                           ψ
             = \rho v = \text{mass flux}
m.
             = Mach number
M
                                                                                                     = angular frequency 2\pi f
             = pressure sensitivity index for steady-state burning,
                                                                                                        dimensionless angular frequency \omega/\bar{k}\bar{v}
n
                                                                                          Ω
                    (\bar{P}/\bar{m})(\partial \bar{m}/\partial \bar{P})_{T_c}
                                                                                              )ь
                                                                                                         conditions far enough from the propellant surface
             = frequency dependent function for a radiating gas
                                                                                                           that the burnt gas properties have assumed
                    analogous to the constant n for a nonradiating
                                                                                                           asymptotic values
                    gas [see Eqs. (20a) and (20b)]
                                                                                                        solid properties far from surface
                                                                                              )<sub>c</sub>
             = pressure
                                                                                               )_f
                                                                                                        downsteam edge of flame zone
                net radiative heat flux directed toward the solid
                                                                                                        homogeneous solution to acoustic differential equa-
                                                                                              )_h
                heat of combustion (positive for exothermic reac-
                    tion)
                                                                                                        particular solution to acoustic differential equation
                                                                                              )_p
R
                molar gas constant
                                                                                          (
                                                                                                        solid phase
                                                                                              )_s
             = reflection coefficient of solid propellant surface
                                                                                              )0
                                                                                                        solid-gas interface
                                                                                                        "cold" side of chemical reaction zone in solid (see
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of Naval Weapons, Department of the Navy, under Contract
                                                                                          (~)
                                                                                                        steady state
No. NOw 62-0604-c.
                                                                                                    = Fourier component; i.e., F = \text{real } [\tilde{F}e^{i\omega t}]
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                                                                                             )<sup>(0)</sup> = zero-order solution for time-dependent quantities
Member AIAA.
                                                                                              )(1)
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                                                                                                   = first-order perturbation (in \zeta_0 e^{sz}) solution for time de-
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pendent quantities

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I. Introduction

WHETHER combustion instability occurs in rocket motors and test apparatuses is determined largely by the propellant response function.1 Much experimental and theoretical effort has been devoted to understanding propellant response. Although many practical problems (mostly those associated with assessing acoustic losses in test cavities) still hinder accurate experimental determinations, considerable progress has been made. Theoretical studies 1-3 of solid propellant response are characterized by many gross approximations, but have predicted an order-of-magnitude behavior with frequency, which agrees rather well with much of the experimental data.4 Unfortunately, not all of the physical parameters required by the theoretical analysis are known, so that a quantitative comparison with experiment is not possible. Nevertheless, it does appear that the acoustic response of at least some propellants is significantly larger, at low frequencies for low operating pressures, than would be expected on the basis of existing theoretical analyses.

At least a partial resolution of this deficiency by the extension of existing theory is the goal of the present paper. In the basic theory of Ref. 1, many well known effects (specie diffusion, order of reaction, thermal radiation, propellant inhomogeneity, etc.) are neglected, and the inclusion of any one effect might substantially modify the result. However, the relevant addition to the theory must be important at low frequencies when the pressure is low. The analysis of the present paper suggests that thermal radiation from the hot propellant gas may offer an explanation for the apparent discrepancy between theory and experiment. The physical reasons underlying the choice of thermal radiation effects as a desirable modification to the existing theory are discussed at length elsewhere⁵ and are not repeated here since this paper is concerned primarily with the analytical aspects of the problem. The ultimate goal of the current analysis is the calculation of the propellant response function at the burning surface for a thermally radiating gas at low frequency. To attain this goal, the model of Ref. 1 is re-examined using relevant modifications for a radiating gas at low frequency. (The analytical methods suited to the low frequency approximation are those of Ref. 2.)

To facilitate analysis, the simplified model of Fig. 1 is utilized. Figure 1 shows four zones of interest: 1) the unreacted solid, 2) the solid reaction zone, 3) the gas reaction zone, and 4) that part of the thermally radiating burnt gas zone which is "visible" to the solid propellant surface. The model is identical to that of Refs. 1–3 except that: in zone 4 the gas is assumed to emit and absorb radiation, but in this zone heat conduction is neglected; at the solid surface, the incident radiative flux is partially reflected and partially absorbed in a thin sublayer of zone 2; zone 3 is assumed transparent because it is thin compared to the radiation absorption length; and finally zones 1, 2, and 3 are assumed nonradiating because they are very cold compared to zone 4.

In principle, it is necessary to solve the time-dependent mass, momentum, energy, and radiative flux conservation equations appropriate to each of the zones, and then join these solutions properly at each zone boundary. In order to accomplish the solution, however, various approximations will be made. A realistic detailed treatment of thermal radiation and absorption by the burnt propellant gases is a problem of considerable complexity in itself, and we contemplate with considerable awe the difficulties that would ensue from appending such complexities to the already quite intricate problem of the time-dependent response of burning propellants. As a result, we shall drastically simplify the description of the thermal radiation and absorption properties and regard them as governed by a gray body law, i.e., the absorption coefficient is regarded as independent of the frequency of emitted radiation, and the emission from each volume is represented by the product of the absorption co-

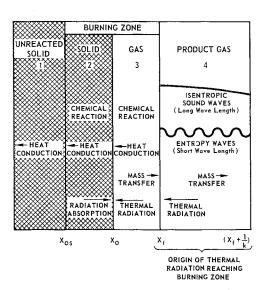


Fig. 1 Schematic model of the burning propellant.

efficient (k) and the emitted radiation from a black body (σ_*T^4) . The departure from steady-state conditions will be assumed small in order that a linear acoustic perturbation treatment will be valid. Further, the solid propellant will be regarded as incompressible, and the other zones will be assumed sufficiently thin that the pressure may be considered uniform across them, and thus we may disregard the momentum conservation equation in the analysis of the acoustic response of these zones. Other approximations will be made and discussed in the text.

II. Mathematical Preliminaries

As has been indicated in the introduction, it will be necessary to obtain linear acoustic perturbation solutions to the mass, energy, and radiative flux conservation equations appropriate to each of the four regions of Fig. 1, and then to join these solutions by application of appropriate boundary conditions. The relevant equations are:

Mass

$$0 = \partial \rho / \partial t + \partial m / \partial x$$

Energy

$$0 = (\partial/\partial t)(\rho C_v T) + (\partial/\partial x)[mH - \lambda G + I^+ - I^-]$$

Positively Directed Radiative Flux

$$0 = \partial I^+/\partial x + k[I^+ - \sigma_* T^4]$$

Negatively Directed Radiative Flux

$$0 = \partial I^-/\partial x - k[I^- - \sigma_* T^4]$$

(In the energy equation, the enthalpy per unit mass H includes the enthalpy of reaction.)

In this section, we shall consider the formulation of the linear acoustic perturbations, and indicate how the solution is to be obtained. Each of the zones of Fig. 1 will be considered in turn.

Zone 1

In the unreacted solid, which is assumed to be incompressible and thermally nonradiating, only the energy conservation equation need be considered. The solution of this equation for zone 1 leads directly to a boundary condition, which will subsequently have to be applied to the next zone. The equation expressing this boundary condition may be obtained from the last equation of the Appendix of Ref. 1

by retaining only the first order acoustic terms and using Fourier notation. Thus\$

$$\lambda_s \widetilde{dG}_{0s} = \overline{m} C_s (\overline{T}_0 - T_c) (\widetilde{\mu}_0 / \Lambda) + \Lambda \overline{m} C_s \overline{T}_0 (d\widetilde{T}_0 / \overline{T}_0) \quad (1)$$

where

$$\Lambda = (\frac{1}{2}) \left[1 + (1 + 4i\omega\tau_s)^{1/2} \right]$$

$$\tau_s = (\lambda_s \rho_s / C_s \overline{m}^2) \qquad \widetilde{\mu}_0 = (\widetilde{dm_0} / \overline{m})$$

Zone 2

The solid phase burning zone is assumed sufficiently thin that there can be no accumulation of mass or energy within the zone. With respect to the absorption of thermal radiation by the surface, we shall assume that all the radiation that is not reflected is completely absorbed in an arbitrarily thin region. With these assumptions, it is again necessary to consider only the energy conservation equation. This equation may be integrated across the zone to yield a relationship between the boundary conditions at the two ends of the zone, namely,

$$\lambda G_0 + g_0 - m_0 C_p T_0 = \lambda_s G_{0s} + m_0 h_v - m_0 C_s T_0 \quad (2a)$$

where

$$h_v = \Delta H(T_0) - (C_v - C_s)T_0 = \Delta H(T_c) - (C_v - C_s)T_c$$

and q_0 is the radiative heat flux absorbed by the surface. Taking the linear perturbation of Eq. (2a) and using the Fourier notation gives

$$\lambda \widetilde{dG_0} + \widetilde{dq_0} = [\overline{m}(C_p \overline{T_0} + h) - \overline{m}C_s(\overline{T_0} - T_c)]\widetilde{\mu_0} + [\overline{m}(C_p - C_s)\overline{T_0}](\widetilde{dT_0}/\overline{T_0}) + \lambda_s \widetilde{dG_{0s}}$$
 (2b)

where $h = h_v - C_s T_c$.

Equation (2b) expresses the boundary condition to be applied to the left-hand boundary of zone 3. It may be expressed in a somewhat more convenient form by eliminating the unknown quantity \widetilde{dG}_{0s} with the aid of Eq. (1):

$$\lambda \widetilde{dG_0} + \widetilde{dq_0} = \overline{m}(C_p \overline{T}_0 + h)(1 - E_1)\widetilde{\mu}_0 + \overline{m}C_p \overline{T}_0 (1 + E_1)(\widetilde{dT_0}/\overline{T}_0) \quad (2c)$$

where

$$E_1 = [(\Lambda - 1)/\Lambda][C_s(\overline{T}_0 - T_c)/(C_p\overline{T}_0 + h)]$$

$$E_2 = (C_s/C_p)(\Lambda - 1)$$

A further relationship expressing the dependence of the gasification rate on the surface temperature and heat input to the surface also will be required. We shall assume that the pyrolysis rate of the solid is some function of the instantaneous values of the surface temperature and of the heat flux incident on the surface. In the linear perturbation approximation, this implies a linear relationship between $\tilde{\mu}_0$, dT_0 , and $(\lambda dG_0 + dq_0)$, which may be expressed in the general form

$$\widetilde{\mu}_0 = \alpha (\lambda \widetilde{dG_0} + \widetilde{dq_0}) / (\lambda \overline{G_0} + \overline{q_0}) + \beta (\widetilde{dT_0} / \overline{T_0})$$
(2d)

where α and β are constant parameters characterizing the solid phase reaction. It is shown in Ref. 1 that in the absence of thermal radiation effects, $\alpha \sim -1$ and $\beta \sim A_s/RT_0$, where A_s is the activation energy for the solid phase reaction, and it may be assumed that these parameters assume equal or comparable values in the presence of radiation.

Zone 3

Since the present paper is concerned primarily with the relatively low frequency domain, it is possible to achieve a

considerable simplification in the analysis by taking advantage of the fact that for not too high frequencies, the period of the acoustic disturbance may be very long compared with the characteristic times associated with the time dependent behavior of this zone. Thus, it will be permissible to carry out an adiabatic treatment of this zone, analogous to that carried out in Ref. 2, and we may assume that the rate of gas phase reaction is some function of the instantaneous values of pressure and temperature gradient at the left-hand boundary of the third zone. In the linear perturbation approximation, this implies a relationship of the form

$$\tilde{\mu}_0 = A\tilde{\epsilon} + B\widetilde{dG_0} \tag{3a}$$

The quantities A and B are found by taking linear variations of appropriate steady-state relationships as in Ref. 2. Details of the evaluation of A and B for the present case are given in the Appendix, where we obtain the results

$$A = -(n/j) [\bar{m}C_s T_c + F_T (C_s T_c / C_p \bar{T}_b) X] / D_{AB}$$
 (3b)

$$B = \lambda X/D_{AB} \tag{3c}$$

$$D_{AB} = \bar{m} \left[\Im \mathcal{C} + C_p \overline{T}_0 / \beta - C_s T_c / j \right] -$$

$$[F_M + F_T C_s T_c / j C_p \overline{T}_b] X \quad (3d)$$

$$X = 1 + \alpha C_p \overline{T}_0 / \beta 30 \tag{3e}$$

where F_M and F_T are given by Eqs. (A3b) and (A3c), and n and j are the respective steady-state burning rate sensitivities to pressure and conditioning temperature [see Eq. (A2)].

The characteristic time considerations of Ref. 1 and the data of the table of Ref. 2 suggest that Eq. (3a) may be valid for frequencies such that

$$\omega \lesssim (\overline{m})^2 C_p / 10 \lambda \overline{\rho}$$

This inequality defines the low frequency regime considered in this paper.

Recapitulation

At this stage of the analysis, it may be helpful to note that Eqs. (2c, 2d, and 3) comprise a set of three linear equations in the five quantities $\tilde{\mu}_0$, $\tilde{\epsilon}$, dT_0 , dG_0 , dq_0 . The pressure amplitude $\tilde{\epsilon}$ may be regarded as an independent variable (since it is the ratio $\tilde{\mu}_0/\tilde{\epsilon}$ which is ultimately to be obtained). Thus, at this stage, there are three linear equations in four unknowns. Of course, the final necessary equation will come from a consideration of the burnt gas region, zone 4.

Zone 4

Solutions for the acoustic field quantities in zone 4 may, of course, be found by consideration of the mass, energy, and radiative flux equations. However, it appears to be convenient to replace the energy equation with the equation for conservation of entropy, i.e.,

$$0 = \rho T(\partial S/\partial t) + mT(\partial S/\partial x) + (\partial/\partial x)[I^{+} - I^{-}]$$
 (4a)

When the mass, entropy, and radiative flux equations are solved simultaneously in zone 4, the dimensionless Fourier component of the entropy at the upstream end of zone 4 (subscript f) $\tilde{\theta}_f$ can be obtained directly as a function of $\tilde{\epsilon}$, and $\tilde{\mu}_f$ and dq_f . These quantities may be expressed in terms of the unknown quantities considered previously.

In order to carry out the linear perturbation about the steady state, it is convenient to define new variables to represent the perturbed quantities:

$$\rho = \bar{\rho}(1+\sigma) \qquad m = \bar{m}(1+\mu) \qquad S = \bar{S} + C_p \theta$$

$$I^+ = \bar{I}^+(1+\beta^+) \qquad I^- = \bar{I}^-(1+\beta^-) \qquad (4b)$$

$$T = \bar{T}(1+\psi) \qquad P = \bar{P}(1+\epsilon)$$

[§] Observe that the notation here is not always that of Ref. 1.

Some particularly useful relationships obtained by substitution of these definitions into the equation of state $P = \rho RT$ and the definition of the entropy increment $[dS/C_p = (1/\gamma)dP/P - d\rho/\rho]$ are

$$\sigma = \epsilon/\gamma - \theta$$
 $\psi = \theta + [(\gamma - 1)/\gamma]\epsilon$ (4c)

Finally, since the absorption coefficient is proportional to density, $k = \bar{k}(1 + \sigma)$.

The equations expressing conservation of radiation flux are somewhat complicated by the fact that the absorption coefficient is proportional to gas density. This complication is easily removed by introducing a new variable z defined by

$$z = \int_0^x \bar{k} \, dx \tag{4d}$$

With this transformation and the preceding definitions, the acoustic perturbation of the conservation equations leads to

$$0 = i\Omega(\tilde{\epsilon}/\gamma - \tilde{\theta}) + d\tilde{\mu}/dz \tag{4e}$$

$$0 = \overline{m}C_{p}\overline{T}(i\Omega\tilde{\theta} + d\tilde{\theta}/dz) + \overline{m}C_{p}(d\overline{T}/dz)\{\tilde{\mu} + \tilde{\theta} +$$

$$[(\gamma - 1)/\gamma]\tilde{\epsilon}\} + (d/dz)(\bar{I}^{+}\tilde{g}^{+} - \bar{I}^{-}\tilde{g}^{-}) \quad (4f)$$

$$0 = (d/dz)(\bar{I}^{+}\mathcal{G}^{+}) + \bar{I}^{+}\tilde{\mathcal{G}}^{+} - 4\sigma_{*}\bar{T}^{4}\{\tilde{\theta}^{+} +$$

$$[(\gamma - 1)/\gamma]\tilde{\epsilon}\} - (\tilde{\epsilon}/\gamma - \tilde{\theta})(d\bar{I}^+/dz)$$
 (4g)

$$0 = (d/dz)(\bar{I}^{-}\tilde{g}^{-}) - \bar{I}^{-}\tilde{g}^{-} + 4\sigma_{*}\bar{T}^{4}\{\tilde{\theta} +$$

$$[(\gamma - 1)/\gamma]\tilde{\epsilon}\} - (\tilde{\epsilon}/\gamma - \tilde{\theta})(d\bar{I}^-/dz)$$
 (4h)

where $\Omega=(\omega/\bar{v}\bar{k})$. (Note that Ω is independent of z.) In deriving Eq. (4f), the relationship $(d\bar{S}/dz)=(C_v/\bar{T})(d\bar{T}/dz)$ is utilized, which is obtained because the steady-state pressure \bar{P} is independent of position. Equations (4e–4h) are four linear first-order nonhomogeneous differential equations with variable coefficients in the dependent variables $\bar{\theta}$, $\tilde{\mu}$, \tilde{g}^+ , and \bar{g}^- . (The equations are nonhomogeneous because $\tilde{\epsilon}$ plays the role of an independent parameter.)

The method of analysis begins with appropriate manipulation of the first-order differential equations [Eqs. (4e-4h)] to eliminate the variables $(\bar{I}^{+}\tilde{g}^{+})$ and $(\bar{I}^{-}\tilde{g}^{-})$ to obtain a third-order nonhomogeneous differential equation in $\tilde{\theta}$ and $\tilde{\mu}$ only. The resulting equation is then solved simultaneously with Eq. (4e) to obtain solutions for $\tilde{\theta}$ and $\tilde{\mu}$. Solutions for the perturbed radiative fluxes can then be obtained by substituting the solutions for $\tilde{\theta}$ and $\tilde{\mu}$.

A simple procedure for obtaining the desired third-order differential equation in $\tilde{\theta}$ and $\tilde{\mu}$ consists of the following three steps: 1) obtain a modified form of Eq. (4f) by eliminating flux derivatives with Eqs. (4g) and (4h) and the steady-state flux equations; 2) differentiate the modified equation twice, and after each differentiation eliminate flux derivatives as before and eliminate $d\tilde{\mu}/dz$ by using Eq. (4e); and 3) eliminate the time-dependent fluxes from the resulting third-order equation by using the modified form of Eq. (4f) obtained in step 1. The term $(\bar{I}^+ + \bar{I}^-)$, which appears in the result, is eliminated by using the relationship $(\bar{I}^+ + \bar{I}^-) = [\bar{m}C_p(d\bar{T}/dz) + 2\sigma_*\bar{T}^4]$. (This relationship follows directly from the steady state forms of the conservation equations for energy and radiative flux.) When the equation that follows from this procedure is divided by $\bar{m}C_p\bar{T}_b$, the result is

where $\delta \equiv (\sigma_* \bar{T}_b^4/\bar{m}C_p\bar{T}_b)$. Examination of Eq. (4i) shows that it is clearly impossible to continue the solutions for the acoustic fields without obtaining the dependence of the steady-state temperature and net radiative flux (9) on position.

III. Steady-State Radiation

We shall not attempt to obtain a detailed solution of the steady-state problem, for this would open Pandora's box a great deal wider than necessary. Instead, we shall follow the spirit of Refs. 1 and 2 by availing ourselves of the generality that follows from regarding such quantities as the mean burning rate and adiabatic flame temperature (which would be prescribed by a complete steady-state burning theory) as given quantities. Let us begin by considering the "radiation zone," i.e., zone 4. The solution to the mass conservation equation is trivial ($\bar{m} = \text{const}$), so that the problem consists in obtaining the solutions to the equations expressing conservation of energy and radiant flux. In terms of the variable z [see Eq. (4d)], these equations are

$$\bar{m}C_{x}(d\bar{T}/dz) + (d/dz)(\bar{I}^{+} - \bar{I}^{-}) = 0$$
 (5a)

$$d\bar{I}^{+}/dz = -[\bar{I}^{+} - \sigma_{*}\bar{T}^{4}]$$
 (5b)

$$d\bar{I}^-/dz = + [\bar{I}^- - \sigma_* \bar{T}^4]$$
 (5e)

The boundary conditions for $z \rightarrow \infty$ are:

$$\overline{T} \to \overline{T}_b \qquad z \to \infty$$
 (6a)

$$\bar{I}^+ \to \sigma_* \bar{T}_b{}^4 \qquad z \to \infty$$
(6b)

$$\bar{I}^- \to \sigma_* \bar{T}_b{}^4 \qquad z \to \infty$$
 (6e)

where T_b , the steady-state adiabatic flame temperature, may be related to the conditioning temperature, net heat release by chemical reaction by integrating the energy conservation equation across all of the zones to obtain

$$\bar{T}_b = T_c + [Q - \Delta H_v(T_c)]/C_p \qquad (6d)$$

(where Q is the heat release per unit mass due to gas phase reactions).

A single differential equation for \bar{T} may be obtained by substituting $d\bar{I}^+/dz$ and $d\bar{I}^-/dz$ from Eqs. (5b) and (5c) into Eq. (5a), differentiating the result and eliminating the $d\bar{I}/dz$ terms with Eqs. (5b) and (5c), and then differentiating the result and subtracting Eq. (5a). One obtains

$$\overline{m}C_{p}(d^{3}\overline{T}/dz^{3}-d\overline{T}/dz)+8\sigma_{*}\overline{T}^{3}(d^{2}\overline{T}/dz^{2})+24\sigma_{*}\overline{T}^{2}(d\overline{T}/dz)^{2}=0$$
 (7a)

In order to obtain an approximate solution to this equation, we shall regard the effect of radiative transfer on the temperature distribution of zone 4 as a perturbation. If there were no radiative effect, T would be spatially uniform, so that we define a perturbation variable ζ by the relationship

$$\overline{T} = \overline{T}_b(1+\zeta) \qquad [\text{or } \zeta = (\overline{T} - \overline{T}_b)/\overline{T}_b] \qquad (7b)$$

and substitute Eq. (7b) into Eq. (7a), to find

$$\frac{d^2\zeta}{dz^3} - \frac{d\zeta}{dz} + \delta[8(1+\zeta)^3(\frac{d^2\zeta}{dz^2}) +$$

$$24(1 + \zeta)^2 (d\zeta/dz)^2] = 0 \quad (7c)$$

$$0 = \frac{\overline{T}}{\overline{T_b}} \left[\frac{d^3 \tilde{\theta}}{dz^3} + i\Omega \frac{d^2 \tilde{\theta}}{dz^2} - \frac{d\tilde{\theta}}{dz} - i\Omega\tilde{\theta} \right] + \frac{d^2 \tilde{\theta}}{dz^2} \left[\frac{4}{\overline{T_b}} \frac{d\overline{T}}{dz} + 8\delta \left(\frac{\overline{T}}{\overline{T_b}} \right)^4 \right] +$$

$$\frac{d\tilde{\theta}}{dz} \left[\frac{3i\Omega}{T_b} \frac{d\overline{T}}{dz} + \frac{3}{\overline{T_b}} \frac{d^2 \overline{T}}{dz^2} + \frac{3\overline{q}}{\overline{m}C_p T_b} + 48\delta \left(\frac{\overline{T}}{T_b} \right)^3 \left(\frac{1}{T_b} \frac{d\overline{T}}{dz} \right) \right] + \tilde{\theta} \left[\frac{3i\Omega}{T_b} \frac{d^2 \overline{T}}{dz^2} + \frac{1}{T_b} \frac{d^3 \overline{T}}{dz^3} + 72\delta \left(\frac{\overline{T}}{T_b} \right)^2 \left(\frac{1}{T_b} \frac{d\overline{T}}{dz} \right)^2 +$$

$$24\delta \left(\frac{\overline{T}}{T_b} \right)^3 \left(\frac{1}{T_b} \frac{d^2 \overline{T}}{dz^2} \right) + \frac{1}{T_b} \frac{d\overline{T}}{dz} \right] + \frac{\tilde{\epsilon}}{\gamma} \left[-\frac{2i\Omega}{T_b} \frac{d^2 \overline{T}}{dz^2} + 24\delta \left(\frac{\overline{T}}{T_b} \right)^2 \left(\frac{1}{T_b} \frac{d\overline{T}}{dz} \right)^2 + 8\delta \left(\frac{\overline{T}}{T_b} \right)^3 \left(\frac{1}{T_b} \frac{d^2 \overline{T}}{dz^2} \right) - \frac{2}{T_b} \frac{d\overline{T}}{dz} \right] +$$

$$\left(\frac{\gamma - 1}{\gamma} \right) \tilde{\epsilon} \left[\frac{1}{T_b} \frac{d^3 \overline{T}}{dz^3} - \frac{1}{T_b} \frac{d\overline{T}}{dz} + 32\delta \left(\frac{\overline{T}}{T_b} \right)^3 \left(\frac{1}{T_b} \frac{d^2 \overline{T}}{dz^2} \right) + 96\delta \left(\frac{\overline{T}}{T_b} \right)^2 \left(\frac{1}{T_b} \frac{d\overline{T}}{dz} \right)^2 \right] + \tilde{\mu} \left[\frac{1}{T_b} \frac{d^3 \overline{T}}{dz^3} - \frac{1}{T_b} \frac{d\overline{T}}{dz} \right]$$

$$(4i)$$

(10b)

We shall begin by retaining, in Eq. (7c), only those terms which are linear in ζ , i.e.,

$$d^3\zeta/dz^3 - d\zeta/dz + 8\delta(d^2\zeta/dz^2) \approx 0$$
 (8a)

(It may be noted that δ is representative of the ratio of radiatively transported energy flux to the connectively transported energy flux, and may be presumed to be small under conditions such that radiative energy transport may be regarded as a perturbing influence.) The relevant solution of Eq. (8a) is

$$\overline{T} \approx \overline{T}_b \{1 + [(\overline{T}_f - \overline{T}_b)/\overline{T}_b]e^{sz}\} = \overline{T}_b [1 + \zeta_0 e^{sz}]$$
 (8b) where $\zeta_0 = (\overline{T}_f - \overline{T}_b)/\overline{T}_b$, and s is the negative root of $s^2 - 1 + 8\delta s = 0$, i.e.,

 $s = -(1 + 4\delta + 8\delta^2) + \text{terms proportional to } \delta^4$ (8c) The quantity ζ_0 is just the fractional increment to the burnt

$$\zeta_0 = (1 - R_*)\delta + 2(1 - R_*)^2\delta^2 + 0(\delta^3)$$
 (9e)

Equation (8b) for \overline{T} and Eq. (9a) for \overline{q} , with ζ_0 given by Eq. (9e), constitute the expressions for the steady-state quantities that are required for the time-dependent formalism as given by Eq. (4i).

IV. Acoustic Solutions in Zone 4

Now that we have the necessary state-state solutions, we may return to the acoustic calculations in zone 4 in order to obtain a fourth equation to solve simultaneously with Eqs. (2c, 2d, and 3a), which will make possible the calculation of $\tilde{\mu}_0/\tilde{\epsilon}$. We must simultaneously solve Eqs. (4e) and (4i). When the expressions for T and \bar{q} of the previous section are substituted into Eqs. (4i), and terms with coefficients of higher order than δ^2 are dropped, these two equations may be expressed in matrix form by:

 $\left. \begin{array}{l} C_2 = 4s + i\Omega + 32\delta \\ C_1 = 5s^2 + 3i\Omega s + 64\delta s \\ C_0 = 2s^3 + (3s^2 - 1)i\Omega + 32\delta s^2 \end{array} \right\}$

We note that the ζ_0e^{sz} terms arise in Eq. (10a) because the

steady-state temperature profile in zone 4 is not flat as it would be for a nonradiating gas. Instead, there is a (small)

"hump" of magnitude $\zeta_0 e^{sz}$ in this profile. In order to obtain

an approximate solution to Eq. (10a), we shall take advantage

of the fact that the radiation hump is small by first deter-

mining the solution that would pertain in the absence of the

temperature hump, and then correcting that solution by

evaluating the perturbation caused by the hump. This will

permit us rather easily to develop an approximation which

The solution that would pertain in the absence of the hump

will be referred to as the "zero-order" solution. In order to

determine it, the $\zeta_0 e^{sz}$ terms of Eq. (10a) are dropped. Then

$$0 = \begin{bmatrix} d/dz & -i\Omega \\ 0 \left[(d^2/dz^2 - 1)(d/dz + i\Omega) + 8\delta(d^2/dz^2) \right] \end{bmatrix} \begin{bmatrix} \tilde{\mu} \\ \tilde{\theta} \end{bmatrix} + \begin{bmatrix} i\Omega \\ 0 \end{bmatrix} \frac{\tilde{\epsilon}}{\gamma} + \begin{bmatrix} 0 \\ -8\delta s^2 \end{bmatrix} \begin{bmatrix} (d^3/dz^3) + C_2(d^2/dz^2) + C_1(d/dz) + C_0 \end{bmatrix} \begin{bmatrix} \tilde{\mu} \\ \tilde{\theta} \end{bmatrix} + \begin{bmatrix} 0 \\ -(s^3 + s + 2i\Omega s^2) \end{bmatrix} \frac{\tilde{\epsilon}}{\gamma} + \begin{bmatrix} 0 \\ 24\delta s^2 \end{bmatrix} (\gamma - 1) \tilde{\epsilon}$$
(10a)

where

gas temperature near the "flame," which arises because of the absorption of thermal radiation by the propellant surface. Integration of the energy conservation equation across zone 4 (neglecting the thermal conductivity in this region, as discussed earlier), yields

$$\zeta_0 = (\bar{T}_f - \bar{T}_b)/\bar{T}_b = \bar{q}_0/\bar{m}C_x\bar{T}_b \tag{8d}$$

It will turn out, as one would probably expect, that when δ is small, ζ_0 is proportional to δ . As a result, when Eq. (8b) is substituted into Eq. (7c), we see that the solution as expressed by Eq. (8b) is actually valid through the terms of order δ^2 . This degree of approximation will suffice for the present analysis, and, when ζ_0 is evaluated, will provide us with the mean temperature distribution, which is required for the evaluation of the time-dependent response as described by Eq. (4i).

Let us now turn our attention to the radiative flux equations in order to obtain expressions for \bar{q} and to evaluate ζ_0 . Noting that $\bar{q} \equiv (\bar{I}^- - \bar{I}^+)$, we integrate Eq. (5a) to obtain

$$\bar{q}/\bar{m}C_x\bar{T}_b = \zeta_0 e^{sz}$$
 (9a)

 $\mathcal{L}_p T_b = \zeta_0 e^{sz} \tag{9a}$

$$0 = \begin{bmatrix} d/dz & -i\Omega \\ 0[(d^2/dz^2 - 1)(d/dz + i\Omega) + 8\delta(d^2/dz^2)] \end{bmatrix} \begin{bmatrix} \tilde{\mu}^{(0)} \\ \tilde{\theta}^{(0)} \end{bmatrix} + \begin{bmatrix} i\Omega \\ 0 \end{bmatrix} \frac{\tilde{\epsilon}}{\tilde{\gamma}}$$
(11a)

Zero-Order Solution

will be valid through δ^2 terms.

 θ and μ satisfy the differential equation

which takes care of the form of \bar{q} . Evaluation of ζ_0 is not quite so simple.

The solution to Eqs. (5a, 5b, and 5c) is not specified entirely by the boundary conditions at $z \to \infty$ [as given by Eqs. (6a, 6b, and 6c)], because it depends also on the fraction of radiant energy which is absorbed by the propellant surface. Thus, we shall characterize the surface by a reflection coefficient R_* , viz.,

$$\bar{I}_0^+ = R_* \bar{I}_0^- \text{ or } \bar{q}_0 = (1 - R_*) \bar{I}_0^-$$
 (9b)

Equations (5b) and (5c) are easily integrated (using an obvious integrating factor for each equation). Each solution consists of a particular integral and a solution to the homogeneous equation. When these solutions are substituted into Eq. (5a), it is found that the coefficients of the homogeneous solutions must be equated to zero, and one obtains

$$\bar{I}^{+}/\bar{m}C_{p}\bar{T}_{b} = \delta\{1 + [4\zeta_{0}/(s+1)]e^{sz}\} + 0(\delta^{3})$$
 (9c)

$$\bar{I}^{-}/\bar{m}C_{p}\bar{T}_{b} = \delta\{1 - [4\zeta_{0}/(s-1)]e^{sz}\} + 0(\delta^{3})$$
 (9d)

The general solution will be the sum of a particular solution and a solution of the homogeneous equation. Particular solutions are easily found to be

$$\theta_p^{(0)} = 0$$
 $\mu_p^{(0)} = -i\Omega z(\tilde{\epsilon}/\gamma)$ (11b)

where the subscript p denotes the particular solution. The homogeneous equations are constant coefficient differential equations, whose solutions will be of the form $e^{s_{p}z}$. Thus, we will write

$$\tilde{\mu}^{(0)} = \mu_p^{(0)} + \sum_{n} \mu_{h\nu}^{(0)} e^{s_{\nu}z}$$

and a similar equation for $\tilde{\theta}^{(0)}$. (In these expressions, the $\mu_{h\nu}{}^{(0)}$ are constants.) The zero-order homogeneous solutions obey the equation

$$0 = \begin{bmatrix} s_{\nu} & -i\Omega \\ 0 & (s_{\nu}^{2} - 1)(s_{\nu} + i\Omega) + 8\delta s_{\nu}^{2} \end{bmatrix} \begin{bmatrix} \mu_{h\nu}^{(0)} \\ \theta_{h\nu}^{(0)} \end{bmatrix}$$
(11c)

where the subscript h denotes the solution of the homogeneous equation. To obtain solutions such that $\mu_{h\nu}^{(0)}$ and $\theta_{h\nu}^{(0)}$ do

not vanish identically, the determinant of the coefficients must vanish, giving the dispersion equation

$$s_{\nu}[(s_{\nu}^2 - 1)(s_{\nu} + i\Omega) + 8\delta s_{\nu}^2] = 0$$
 (11d)

to which there are four roots. One of these roots has a positive real part that can arise only from a downstream source and is thus not physically allowable for the present problem. The remaining roots are (to order δ^2)

$$s_2=0$$

$$s_3=-i\Omega(1+\Delta_3)$$

$$s_4=-(1+\Delta_4)$$
 (11e)

where

$$\Delta_3 = -[8\delta i\Omega/(1+\Omega^2)][1-16\delta i\Omega/(1+\Omega^2)^2]$$

$$\Delta_4 = [4\delta/(1-i\Omega)][1+2\delta(1-3i\Omega)/(1-i\Omega)^2]$$

If the pressure had not been taken uniform over zone 4, the root s_2 would have been split into two (nonzero) roots corresponding to left and right traveling acoustic waves (cf. Ref. 3). The root s_3 represents the traveling entropy wave discussed, for a nonradiating gas, in Ref. 3. The root s_4 represents a highly damped solution peculiar to radiating gases.

The relationships between the zero-order solutions of the homogeneous equation are readily found using Eq. (11a), namely,

$$\mu_{h3}^{(0)} = (i\Omega/s_3)\theta_{h3}^{(0)}$$

$$\mu_{h4} = (i\Omega/s_4)\theta_{h4}^{(0)} \qquad \theta_{h2}^{(0)} = 0$$
(11f)

Perturbation Solutions

Now we shall perturb each of the zero-order (no "hump") solutions by taking into account the terms that arise from the temperature "hump." It may easily be verified that to second order in δ , the solution for $\tilde{\mu}$ and $\tilde{\theta}$ may be written in the form

$$\tilde{\mu} = \mu_{p}^{(0)} + \mu_{p}^{(1)} \zeta_{0} e^{sz} + \sum_{n=2,3,4} \left[\mu_{h\nu}^{(0)} e^{s\nu z} + \zeta_{0} \mu_{h\nu}^{(1)} e^{(s\nu + s)z} \right]$$

with an analogous expression for $\tilde{\theta}$. Here, $\mu_p^{(0)}$ and $\mu_p^{(1)}$ will be functions of z, in general, but $\mu_{h\nu}^{(0)}$ and $\mu_{h\nu}^{(1)}$ are constants. The equations satisfied by the perturbed quantities are readily found to be

$$\theta_{h2}^{(1)} = -(s/i\Omega)\mu_{h2}^{(0)} \tag{12d}$$

$$\mu_{h\nu}^{(1)}/\theta_{h\nu}^{(0)} = \left[i\Omega/(s_{\nu} + s)\right]\theta_{h\nu}^{(1)}/\theta_{h\nu}^{(0)}$$

$$[\nu = 3, 4] \quad (12e)$$

$$\mu_{h2}^{(1)} = -\mu_{h2}^{(0)} \tag{12f}$$

$$\theta_{p}^{(1)} = sz(\tilde{\epsilon}/\gamma) + (3s/i\Omega)[(\gamma - 1)/\gamma]\tilde{\epsilon}$$
 (12g)

$$\mu_{v}^{(1)} = (i\Omega z - i\Omega/s)(\tilde{\epsilon}/\gamma) + 3[(\gamma - 1)/\gamma]\tilde{\epsilon}$$
 (12h)

The preceding equations show that the solutions for $\tilde{\theta}$ and $\tilde{\mu}$ to order δ^2 are

$$\tilde{\theta} = -\mu_{h2}^{(0)} \left[\left(\frac{s}{i\Omega} \right) \zeta_0 e^{sz} \right] + \left\{ \sum_{\nu=3,4} \theta_{h\nu}^{(0)} e^{s\nu z} \times \left[1 + \left(\frac{\theta_{h\nu}^{(1)}}{\theta_{h\nu}^{(0)}} \right) \zeta_0 e^{sz} \right] \right\} + \zeta_0 e^{sz} \left[sz \left(\frac{\tilde{\epsilon}}{\gamma} \right) + \left(\frac{3s}{i\Omega} \right) \left(\frac{\gamma - 1}{\gamma} \right) \tilde{\epsilon} \right]$$
(13a)

$$\tilde{\mu} = \mu_{h3}^{(0)} [1 - \zeta_0 e^{sz}] + \left\{ \sum_{\nu=3,4} \left(\frac{i\Omega}{s_{\nu}} \right) \theta_{h\nu}^{(0)} e^{s_{\nu}z} \times \left[1 + \left(\frac{s_{\nu}}{(s_{\nu} + s)} \right) \left(\frac{\theta_{h\nu}^{(1)}}{\theta_{h\nu}^{(0)}} \right) \zeta_0 e^{sz} \right] \right\} - i\Omega z \left(\frac{\tilde{\epsilon}}{\gamma} \right) + \zeta_0 e^{sz} \times \left[\left(i\Omega z - \frac{i\Omega}{s} \right) \left(\frac{\tilde{\epsilon}}{\gamma} \right) + 3 \left(\frac{\gamma - 1}{\gamma} \right) \tilde{\epsilon} \right]$$
(13b)

It should be noted that the perturbation method need not be carried beyond this solution, since the next order of approximation will introduce terms proportional to δ^3 . [This follows from the fact that $\bar{T} = \bar{T}_b(1 + \zeta_0 e^{sz} + \delta^3 \text{ terms})$.]

Before the fourth linear relationship that was required in Sec. II can be obtained, the time-dependent radiative fluxes at z=0 must be found. Now Eqs. (4g) and (4h) are easily integrated since we know $\bar{\theta}$, \bar{T} , \bar{I}^+ , and \bar{I}^- . Thus, into Eqs. (4g) and (4h) we substitute $\bar{T} \approx \bar{T}_b(1+\zeta_0e^{sz})$ and [from Eqs. (9c) and (9d)] $d\bar{I}^+/dz = \bar{m}C_p\bar{T}_b[4\zeta_0/(s+1)]e^{sz}$ and $d\bar{I}^-/dz = -\bar{m}C_p\bar{T}_b[(4\zeta_0)/(s-1)]e^{sz}$. [Note that care must be exercised in connection with $d\bar{I}^+/dz$, since $\zeta_0/(s+1)$ is of order unity rather than ζ_0 .] As a result, the solution for $\bar{I}^+\bar{g}^+$ turns out to be somewhat more complicated than the solution for $\bar{I}^-\bar{g}^-$. In particular, terms in $[\delta\zeta_0^2/(s+1)]e^{2sz}$ will appear in $\bar{I}^+\bar{g}^+$, whereas $[\delta\zeta_0^2/(s-1)]e^{2sz}$ terms are of order δ^3 , and thus need not be retained in solving for $\bar{I}^-\bar{g}^-$].

$$0 = \begin{bmatrix} (s_{\nu} + s) & -i\Omega \\ 0 & \{ [(s_{\nu} + s)^{2} - 1](s_{\nu} + s + i\Omega) + 8\delta(s_{\nu} + s)^{2} \} \end{bmatrix} \begin{bmatrix} \mu_{h\nu}^{(1)} \\ \theta_{h\nu}^{(1)} \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ -8\delta s^{2} & [s_{\nu}^{3} + C_{2}s_{\nu}^{2} + C_{1}s_{\nu} + C_{0}] \end{bmatrix} \begin{bmatrix} \mu_{h\nu}^{(0)} \\ \theta_{h\nu}^{(0)} \end{bmatrix}$$
(12a)
$$0 = \begin{bmatrix} d/dz & -i\Omega \\ 0 & [(d^{2}/dz^{2} - 1)(d/dz + i\Omega) + 8\delta(d^{2}/dz^{2})] \end{bmatrix} \begin{bmatrix} \mu_{p}^{(1)}e^{sz} \\ \theta_{p}^{(1)}e^{sz} \end{bmatrix} + e^{sz} \begin{cases} \begin{bmatrix} 0 & 0 \\ -8\delta s^{2} & [d^{3}/dz^{3} + C_{2}(d^{2}/dz^{2}) + C_{1}(d/dz) + C_{0}] \end{bmatrix} \times \\ \begin{bmatrix} \mu_{p}^{(0)} \\ \theta_{p}^{(0)} \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ -8\delta s^{2} & [d^{3}/dz^{3} + C_{2}(d^{2}/dz^{2}) + C_{1}(d/dz) + C_{0}] \end{bmatrix} (12b)$$

The solutions to Eqs. (12a) and (12b) are

$$\frac{\theta_{h\nu}^{(1)}}{\theta_{h\nu}^{(0)}} = \frac{(-)[s_{\nu}^{4} + C_{2}s_{\nu}^{3} + C_{1}s_{\nu}^{2} + C_{0}s_{\nu} - i\Omega 8\delta s^{2}]}{s_{\nu}[((s_{\nu} + s)^{2} - 1)(s_{\nu} + s + i\Omega) + 8\delta(s_{\nu} + s)^{2}]}$$

$$[\nu = 3, 4] \quad (12c)$$

As in the steady-state case, particular and homogeneous solutions are obtained for $\bar{I}^{+}\bar{g}^{+}$ and $\bar{I}^{-}\tilde{g}^{-}$, and again the coefficient of the homogeneous solutions must be set equal to zero. The final result (as may easily be verified by substitution) is

$$\frac{\bar{I}^{+}\bar{\theta}^{+}}{\bar{m}C_{p}\bar{T}_{b}} = \frac{4\delta\zeta_{0}se^{sz}}{s+1} \left[z - \frac{\zeta_{0}s[(2s+1)z-1]e^{sz}}{(2s+1)^{2}} \right] \frac{\tilde{\epsilon}}{\gamma} + 4\delta \left[1 + \frac{3\zeta_{0}se^{sz}}{i\Omega(s+1)} + \frac{4\zeta_{0}e^{sz}}{s+1} - \frac{3s^{2}\zeta_{0}^{2}e^{2sz}}{i\Omega(s+1)(2s+1)} \right] \left(\frac{\gamma-1}{\gamma} \right) \tilde{\epsilon} - \frac{4\delta\zeta_{0}se^{sz}}{i\Omega(s+1)} \left[1 - \frac{s\zeta_{0}e^{sz}}{2s+1} \right] \mu_{h2}^{(0)} + 4\delta \sum_{\nu=3,4} e^{s_{\nu}z}\theta_{h\nu}^{(0)} \left\{ \frac{1}{s_{\nu}+1} + \frac{4\zeta_{0}e^{sz}}{s_{\nu}+s+1} - \frac{s\zeta_{0}e^{sz}}{(s+1)(s_{\nu}+s+1)} + \frac{\theta_{h\nu}^{(1)}}{\theta_{h\nu}^{(0)}} \left[\frac{\zeta_{0}e^{sz}}{(s_{\nu}+s+1)} - \frac{s\zeta_{0}^{2}e^{2sz}}{(s+1)(s_{\nu}+2s+1)} \right] \right\} (14a)$$

$$\frac{\bar{I}^{-\check{g}^{-}}}{\bar{m}C_{p}T_{b}} = -\frac{4\delta\zeta_{0}sze^{sz}}{s-1} \left(\frac{\tilde{\epsilon}}{\gamma}\right) + 4\delta \left[1 - \frac{3\zeta_{0}se^{sz}}{i\Omega(s-1)} - \frac{4\zeta_{0}e^{sz}}{s-1}\right] \left(\frac{\gamma-1}{\gamma}\right) \tilde{\epsilon} + \frac{4\zeta_{0}e^{sz}}{i\Omega(s-1)} \mu_{h2}^{(0)} - 4\delta \sum_{\nu=3,4} e^{s\nu\bar{z}}\theta_{h\nu}^{(0)} \left\{\frac{1}{s_{\nu}-1} + \frac{4\zeta_{0}e^{sz}}{s_{\nu}+s-1} - \frac{s\zeta_{0}e^{sz}}{(s-1)(s_{\nu}+s-1)} + \frac{\theta_{h\nu}^{(1)}}{\theta_{h\nu}^{(0)}} \frac{\zeta_{0}e^{sz}}{(s_{\nu}+s-1)}\right\} (14b)$$

When Eqs. (13a, 13b, 14a, and 14b) are evaluated at z=0, and when it is recognized that

0, and when it is recognized that
$$\widetilde{dq_0} = \bar{I}_0 - \tilde{g}^- - \bar{I}_0 + \tilde{g}^+ = (1 - R_*)\bar{I}_0 - \tilde{g}^- = [(1 - R_*)/R_*]\bar{I}_0 + \tilde{g}_0 +$$

there are four linear algebraic relations in the seven quantities $\tilde{\theta}_f$, $\tilde{\mu}_0$, $\overline{dq_0}/\overline{m}C_p\overline{T}_b$, $\tilde{\epsilon}$, $\theta_{h3}^{(0)}$, $\theta_{h4}^{(0)}$, and $\mu_{hz}^{(0)}$. From these equations, the last three quantities can be eliminated to obtain a linear relationship among the other four. This is a tedious, but straightforward, procedure that is not repeated here. To second order in δ , the relationship is

$$0 = \frac{\widetilde{dq_0}}{\overline{m}C_pT_b} \left\{ 1 + \delta \left(\frac{4i\Omega(3+i\Omega)}{(1+i\Omega)(1-i\Omega)^2} - \zeta_0 \left(\frac{2i\Omega}{1+i\Omega} \right) \right\} - \widetilde{\theta}_f \left\{ \frac{4\zeta_0}{1+i\Omega} + \delta\zeta_0 \left(\frac{32i\Omega(1+3i\Omega)}{(1+i\Omega)^3(1-i\Omega)^2} \right) - \zeta_0^2 \left(\frac{12}{(1+i\Omega)(2+i\Omega)} \right) \right\} - \frac{\gamma-1}{\gamma} \widetilde{\epsilon} \times \left\{ 4\zeta_0 + \delta\zeta_0 \left(\frac{16i\Omega(3+i\Omega)}{(1+i\Omega)(1-i\Omega)^2} \right) - \frac{\gamma-1}{\gamma} \widetilde{\epsilon} \right\} \right\}$$

$$0 = \begin{bmatrix} -\zeta_0 \left(\frac{3\mathfrak{C}}{C_p \overline{T}_0} - \frac{\zeta_0}{2} & \overline{T}_b \right) & -\zeta_0 \\ \\ 1 & -\beta \\ \\ \hline 1 & 0 \\ \\ \overline{m} \mathfrak{FC}(1 - E_1) & \overline{m} C_p \overline{T}_0 (1 + E_2) \end{bmatrix}$$

$$\left. \left. \left\langle \zeta_0^2 \left(\frac{2(3+4i\Omega)}{(1+i\Omega)} \right) \right\rangle - \tilde{\mu}_0 \left\{ \frac{2\zeta_0^2}{1+i\Omega} \right\} \right.$$
 (15)

[Since $dq_0/\bar{m}C_p\bar{T}_b$ is of order δ , only terms through the first power of δ need be retained in its coefficient in Eq. (15).]

The essential step remaining in the determination of the required fourth linear equation is the elimination of the

$$\frac{\lambda \widetilde{dG_0}}{\overline{m}C_x\overline{T_0}} \left[\zeta_0 \right] - \widetilde{\mu}_0 \left[\frac{3C\zeta_0}{C_x\overline{T_0}} - \frac{\zeta_0^2}{2} \frac{\overline{T_b}}{\overline{T_0}} \right] \quad (17a)$$

where

$$\xi_1 = (1 + i\Omega)/4 + \delta i\Omega/(1 + i\Omega) +$$

$$\zeta_0(5 + 2i\Omega + \Omega^2)/4(2 + i\Omega)$$
 (17b)

$$\xi_3 = i\Omega + 4\delta i\Omega/(1+i\Omega) - \zeta_0 i\Omega(1+2i\Omega)/2(2+i\Omega)$$
 (17c)

This result is an approximate solution, which is valid only through terms of order δ^2 . We have not expanded the result in powers of δ , however, because this leads to a considerably more unwieldy expression.

Since there are now four linear equations [Eqs. (2c, 2d, 3a, and 17a)] in the 5 quantities dq_0 , $\tilde{\epsilon}$, $\tilde{\psi}_0$, λdG_0 , and $\tilde{\mu}_0$, it is now a simple matter to calculate the propellant response function $\tilde{\mu}_0/\tilde{\epsilon}$.

V. Evaluation of the Response Function

The four equations that are to be solved for $\tilde{\mu}_0/\tilde{\epsilon}$ may now be expressed in the matrix form**

$$\frac{\zeta_{0}}{\overline{m}C_{p}\overline{T}_{0}} \qquad \xi_{1} \\
\frac{-\alpha}{\overline{m}5C} \qquad \frac{-\alpha C_{p}\overline{T}_{0}}{3C} \\
-B/\lambda \qquad 0 \\
-1 \qquad -\overline{m}C_{p}\overline{T}_{0}$$

$$\begin{bmatrix}
\widetilde{\mu}_{0} \\
\widetilde{\psi}_{0} \\
\widetilde{dq}_{0} \\
\overline{m}C_{p}\overline{T}_{0}
\end{bmatrix} - \begin{bmatrix}
\zeta_{0} \frac{\gamma - 1}{\gamma} \frac{\overline{T}_{b}}{\overline{T}_{0}} \xi_{2} \\
0 \\
A \\
0
\end{bmatrix} \widetilde{\epsilon} \qquad (18)$$

Obtaining the result is quite straightforward, and the details need not be presented here. A few intermediate steps will be given, however, to assist the reader who might wish to verify the solution. From Eq. (18), $\tilde{\mu}_0/\tilde{\epsilon}$ may be expressed as the ratio of two fourth-order determinants. Expansion of these determinants, and division of each by $[\beta + \alpha C_p \overline{T}_0(1 + E_2)/5C]$ leads to

$$\frac{\tilde{\mu}_{0}}{\tilde{\epsilon}} = \frac{A(\xi_{1} - \zeta_{0}) - \zeta_{0}\xi_{2} \frac{B\overline{m}C_{p}\overline{T}_{b}}{\lambda} \frac{\gamma - 1}{\gamma}}{\left\{\xi_{1} - \zeta_{0} - \xi_{1} \left(\frac{B\overline{m}\mathfrak{I}\mathfrak{C}}{\lambda}\right) \left[\frac{C_{p}\overline{T}_{0}(1 + E_{2}) + \beta\mathfrak{I}\mathfrak{C}(1 - E_{1})}{\beta\mathfrak{I}\mathfrak{C} + \alpha C_{p}\overline{T}_{0}(1 + E_{2})}\right] + \zeta_{0} \left(\frac{B\overline{m}C_{p}\overline{T}_{0}}{\lambda}\right) \left[\frac{\mathfrak{I}\mathfrak{C}}{C_{p}\overline{T}_{0}} - \frac{\zeta_{0}}{2} \frac{\overline{T}_{b}}{\overline{T}_{0}} + \frac{[1 - \alpha(1 - E_{1})]\mathfrak{I}\mathfrak{C}}{\beta\mathfrak{I}\mathfrak{C} + \alpha C_{p}\overline{T}_{0}(1 + E_{2})}\right\}$$

$$(19a)$$

variable

$$\tilde{\theta}_f = \{ \tilde{\psi}_f - [(\gamma - 1)/\gamma]\tilde{\epsilon} \}$$
 (16a)

and the determination of ψ_f in terms of quantities at the solid-gas interface (subscript 0). This procedure is necessary since the first three linear equations [Eqs. (2c, 2d, and 3a)] are stated in terms of the values assumed by the various unknowns at the burning surface. Integration of the energy equation across zone 3 yields

$$\tilde{\psi}_{f} = (\bar{T}_{0}/\bar{T}_{f})\tilde{\psi}_{0} - \lambda \widetilde{dG}_{0}/\bar{m}C_{p}\bar{T}_{f} + \tilde{\mu}_{0}[(\bar{m}\mathfrak{FC} - \bar{q}_{0})/\bar{m}C_{p}\bar{T}_{f}]$$
 (16b)

Substitution of Eqs. (16a) and (16b) into Eq. (15), using $\overline{T}_f = \overline{T}_b(1 + \zeta_0)$ and $(q_0/\overline{m}C_v\overline{T}_b) = \zeta_0$, and retaining only terms through order δ^2 , gives for the fourth linear equation

$$0 = rac{\widetilde{dq_0}}{\overline{m}C_p\overline{T}_0} \left[\xi_1
ight] - ilde{\epsilon} \left[\zeta_0rac{\overline{T}_b}{\overline{T}_0}rac{\gamma-1}{\gamma}\,\xi_2
ight] - ilde{\psi}_0[\zeta_0] +$$

¶ It should be recalled that the ratios $\theta_{h\nu}^{(1)}/\theta_{h\nu}^{(0)}$ for $\nu=3,4,$ which occur in Eqs. (13) and (14), can be evaluated by Eq. (12c) and are therefore not unknowns.

If we note that

$$\frac{C_{p}\overline{T}_{0}(1+E_{2})+\beta \Im C(1-E_{1})}{\beta \Im C+\alpha C_{p}\overline{T}_{0}(1+E_{2})}=\frac{\beta J_{+}+\beta \Im C+C_{p}\overline{T}_{0}}{\beta \Im C+\alpha C_{p}\overline{T}_{0}} \quad (19b)$$

and

$$\frac{[1 - \alpha(1 - E_1)] \Im \mathcal{C}}{\beta \Im \mathcal{C} + \alpha C_p \overline{T}_0 (1 + E_2)} = -\frac{J_+}{C_p \overline{T}_0} - \frac{\Im \mathcal{C}}{C_p \overline{T}_0} + \frac{\Im \mathcal{C}}{C_p \overline{T}_0} \left[\frac{\beta J_+ + \beta \Im \mathcal{C} + C_p \overline{T}_0}{\beta \Im \mathcal{C} + \alpha C_p \overline{T}_0} \right] \quad (19c)$$

wherett

$$J_+ = C_s(\overline{T}_0 - T_c) \frac{(1-\Lambda)}{\Lambda} +$$

** The first row of the matrix equation is Eq. (17a); the second Eq. (2d), the third Eq. (3a), and the fourth Eq. (2c).

†† The quantity J_+ is identical to the same quantity which appears in Ref. 2 if the solid propellant in Ref. 2 is regarded as incompressible. Our notation is slightly different, however. In Ref. 2, our Λ is denoted by α , and our α has been set equal to -1.

$$C_{s}\overline{T}_{0}(\Lambda-1)\left\{\frac{(1-\alpha)\mathcal{K}+\alpha C_{s}(\overline{T}_{0}-T_{c})(\Lambda-1)/\Lambda}{\beta\mathcal{K}+\alpha C_{p}\overline{T}_{0}+\alpha C_{s}\overline{T}_{0}(\Lambda-1)}\right\}$$
(19d)

and further, if we use the expressions for A, B, ξ_1 , ξ_2 , X, F_T , and F_M , we may express the final result in a form somewhat like that of Ref. 2, viz.,

$$\frac{\tilde{\mu}_0}{\tilde{\epsilon}} = \frac{n_*(\Omega)}{1 + j_*(\Omega)J_+(\omega)/C_*T_c}$$
 (20a)

where

$$n_* = n \left\{ 1 + X \left[\frac{j}{n} \frac{\gamma - 1}{\gamma} \frac{C_p \overline{T}_b}{C_s T_c} \frac{4\zeta_0 i\Omega}{1 + i\Omega} \times \left(1 - 4X\zeta_0 + \frac{4\delta}{(1 + i\Omega)^2} + \frac{\zeta_0 (5 + i\Omega)}{2(1 + i\Omega)(2 + i\Omega)} \right) + j\zeta_0^2 \frac{C_p \overline{T}_b}{C_s T_c} \frac{2i\Omega}{1 + i\Omega} \right] \right\}$$
(20b)

$$j_{*} = j \left\{ 1 - \frac{2i\Omega X}{1 + i\Omega} \left[2\zeta_{0} + \frac{8\delta\zeta_{0}}{(1 + i\Omega)^{2}} + \zeta_{0}^{2} \left(\frac{11 + 10i\Omega - 3\Omega^{2}}{(2 + i\Omega)(1 + i\Omega)} - j \frac{C_{p}\overline{T}_{b}}{C_{s}T_{c}} \right) \right] + 16\zeta_{0}^{2}X^{2} \frac{i\Omega}{1 + i\Omega} \right\}$$
(20c)

The calculations for $\tilde{\mu}_0/\tilde{\epsilon}$ are now complete since J_+ is known from Eq. (19d) and the remaining parameters are fundamental properties of the propellant and its gas, except for ζ_0 , which is given by Eq. (9e). It is rather satisfying to note that in the limit of no radiation $(\delta \to 0, \zeta_0 \to 0)$, or perfect reflection at the burning surface $(R_* \to 1, \zeta_0 \to 0)$, the result as given by Eq. (20a) correctly becomes identical with the result of Ref. 2 for the case of an incompressible propellant and a nonradiating gas.

VI. Discussion

Since the primary purpose of the present paper is the presentation of the details of the calculation of $\tilde{\mu}_0/\tilde{\epsilon}$, and since Ref. 5 discusses the quantitative features of the result in some detail, we shall limit our discussion for the most part to the qualitative aspects of the solution.

As one might expect, the final expression for the mass response of the propellant (i.e., for $\tilde{\mu}_0/\tilde{\epsilon}$) is sufficiently complicated that one must, in general, resort to a numerical study of its implications. There are, however, some features of the effect of radiation which may be obtained by inspection.

First, it may be noted that in the limit of zero frequency, the $n^* \to n$, and $J_+ \to 0$, so that the pressure response of the propellant approaches the steady-state pressure index as it must, because the theory here and in Refs. 1-3 has been carefully constructed so that $\tilde{\mu}_0/\tilde{\epsilon}$ reduces to its empirically observed value (n) at zero frequency regardless of the mechanisms that actually determine n. As the frequency is increased from zero, the radiation terms will begin to become important when the dimensionless frequency $\Omega = \omega/\bar{k}_b\bar{v}_b =$ $\omega/\bar{k}_t\bar{v}_t$ becomes significantly large. (It will be recalled that \bar{k}_f is the reciprocal of the mean absorption length for thermal radiation, and \bar{v}_f is the mean speed of the burnt gas leaving the burning region.) Thus, for an absorption length of, say, 1 cm, and a burnt gas velocity of 500 cm/sec, Ω becomes equal to unity at about 80 cps. It is evident, therefore, that effects of thermal radiation will appear in the low-frequency regime, where theory that neglects radiation may be in difficulty. As has already been mentioned, the radiative effects vanish if the reflection coefficient of the surface is unity, or if $\delta = \sigma_* \bar{T}_b^4 / \bar{m} C_p \bar{T}_b$ is negligibly small. We note that the size of δ decreases with increasing burning rate, and thus the radiative effects will tend to be large in the low pressure regime where the mean burning rate of propellants tends to be small. Thus, radiation effects will evidently tend to be

greatest for just those conditions which are of most concern to us here.

One further observation regarding the solution may be made by considering the frequency domain for which Ω is large, where

$$n_* \to n + 4jX[(\gamma - 1)/\gamma](C_p \overline{T}_b/C_s T_c) \zeta_0 + 2Xj(C_p \overline{T}_b/C_s T_c) \{n - [8(\gamma - 1)/\gamma]X\} \zeta_0^2$$
 (21a)

$$j^* \to j \left[1 - 4X\zeta_0 + 2X\zeta_0^2 (8X + jC_p \overline{T}_b/C_s T_c - 3) \right]$$
 (21b)

(It should be noted that Ω can become reasonably large, and we may still satisfy our approximation that the absorption length is short compared to the acoustic wavelength.) Thus, for such frequencies, the propellant response is given by an expression of the same form that pertains in the absence of thermal radiation, except that n_* and j_* must be used instead of n and j. In this frequency domain, therefore, the qualitative results of the nonradiative theoretical treatments will remain valid.

In order to illustrate in detail the effects that absorption of thermal radiation might have on the propellant response function, we have evaluated Eq. (20a) numerically for several possible values of the parameters. Examples of these results were given in Ref. 5 (Figs. 4 and 5); there we plotted the real part of $\tilde{\mu}_0/\tilde{\epsilon}$, which represents that part of the mass response that is in phase with the pressure, and thus contributes to the amplification or attenuation of sound by the burning propellant. These results show that radiation could indeed be responsible for a considerable enhancement in propellant response in the low frequency regime under conditions when the mean burning rate is relatively low. Unfortunately, the values of the parameters that would be required in order to complete a quantitative comparison with experiment are not available to us.

In conclusion, it seems appropriate to recognize some of the limitations imposed by the approximations we have made. It will be noted that in order to carry through the solution of the basic equations, we have assumed that the influence of thermal radiation was relatively small in order to utilize perturbation methods. It turns out, however, that the radiation effects are not necessarily small. One conclusion that may be drawn from these considerations is that a more realistic treatment of thermal radiation effects is desirable. In view of the complexity of even the present treatment, however, it would seem inadvisable to attempt such a treatment by extending the perturbation approach.

A quantitative estimate of the limit of validity of the present perturbation method may be obtained by estimating the magnitude third-order term in n_* and j_* , and requiring that it should be less than $\frac{1}{10}$. Thus, we will require that the product of the first-and second-order terms in n_* and j_* be less than $\frac{1}{10}$. The requirement on j_* turns out ordinarily to lead to the more severe criterion, namely,

$$v_s > 4.32 (\sigma_* \bar{T}_b^4/\rho_s C_p \bar{T}_b) [j^2 (1 + j C_p \bar{T}_b/C_s T_c)]^{1/3}$$

Thus, for example, if $\bar{T}_b = 2400$ °K, $C_p = C_s = \frac{1}{3}$ cal/gm-°K, $\rho_s = 1.6$ gm/cm³, $T_c = 3000$ °K, j = 1, we estimate that the present perturbation method would become invalid for burning rates less than about 0.13 in./sec.

Appendix

In the preliminary treatment of zone 3 for the timedependent case, it was stated [see Eq. (3a)] that the adiabatic response of that zone to time dependent fluctuations implies a relationship of the form

$$\widetilde{\mu}_0 = A\widetilde{\epsilon} + B\widetilde{dG_0} \tag{A1a}$$

where

$$A = (\bar{P}/\bar{m})(\partial \bar{m}/\partial \bar{P})_{\bar{G}_0} \tag{A1b}$$

$$B = (1/\bar{m})(\partial \bar{m}/\partial \bar{G}_0)_{\bar{P}} \tag{A1c}$$

In this Appendix, we shall calculate A and B.

Four equations are to be utilized in the determination of A and B: 1) the adiabatic relationship between the increments of mass flux, heat input, and temperature at the left-hand boundary of zone 3, i.e., Eq. (2d); 2) the steady-state form of the incremental boundary condition at the left-hand boundary of zone 3; 3) the steady-state perturbed form of the equation expressing the radiant heat flux at the solid gas

where

$$F_M = -\bar{m}C_p \bar{T}_b(2\zeta_0^2) \tag{A3b}$$

$$F_T = \bar{m}C_p\bar{T}_b(4\zeta_0 + 6\zeta_0^2) \tag{A3c}$$

Adiabatic perturbation of Eq. (A2) is trivial. In matrix form, then, the four equations are \S

$$0 = \begin{bmatrix} F_{M} & 0 & (C_{s}T_{c}/C_{p}\bar{T}_{b})F_{T} & -1 & 0 & 0\\ \bar{m}\bar{3}\bar{C} & \bar{m}C_{p}\bar{T}_{0} & -\bar{m}C_{s}T_{c} & -1 & -1 & 0\\ 1 & -\beta & 0 & -\alpha/\bar{m}\bar{3}\bar{C} & -\alpha/\bar{m}\bar{3}\bar{C} & 0\\ 1 & 0 & -j & 0 & 0 & -n \end{bmatrix} \times \begin{bmatrix} d\bar{m}/\bar{m}\\ d\bar{T}_{0}/\bar{T}_{0}\\ dT_{c}/T_{c}\\ d\bar{\zeta}_{0}\\ \lambda d\bar{G}_{0}\\ d\bar{P}/\bar{P} \end{bmatrix}$$
(A4)

interface, i.e., Eq. (9a) evaluated at z=0; and 4) the perturbed form of the empirical steady-state burning rate equation

$$\bar{m} \propto \bar{P}^n T_c{}^j$$
 (A2)

These four equations easily may be expressed in terms of six (unknown) incremental quantities, namely, $d\bar{m}/\bar{m}$, $d\bar{T}_0/\bar{T}_0$, dT_c/T_c , $d\bar{q}_0$, $d\bar{G}_0$, and $d\bar{P}/\bar{P}$. Since [see Eqs. (A1b) and (A1c)] we are looking for the ratio of two of these quantities with a third quantity held fixed, these four equations will suffice. Equation (2d) is already in incremental form. The second equation is easily obtained by incrementing Eq. (2a) and eliminating $d\bar{G}_{0s}$ by using the expression $\lambda_s\bar{G}_{0s}=\bar{m}C_s(\bar{T}_0-T_c)$ which is obtained by integrating the steady-state energy conservation equation from $T=T_c$ to $T=\bar{T}_0$. It will also be necessary to express Eqs. (9a) and (A2) in incremental form. The evaluation of Eq. (9a) at z=0 gives $q_0=\zeta_0\bar{m}C_p\bar{T}_b$. If we use the definition of ζ_0 in Eq. (9e) and note that Eq. (6d) may be adiabatically perturbed to give $C_pd\bar{T}_b=C_sdT_c$, ‡‡ the perturbed form of Eq. (9a) at z=0 is

$$d\bar{q}_0 = F_M(d\bar{m}/\bar{m}) + F_T(C_s T_c/C_n \bar{T}_b)(dT_c/T_c)$$
 (A3a)

where we have used the relationship $3C \equiv C_p T_0 + h = \lambda \bar{G}_0 + \bar{q}_0$.

The coefficients A and B can be obtained from Eq. (A4) by using the definitions of Eqs. (A1b) and (A1c) in a completely straightforward manner to obtain the results stated in Eqs. (3b-3e).

References

¹ Hart, R. W. and McClure, F. T., "Combustion instability: Acoustic interaction with a burning propellant surface," J. Chem. Phys. **30**, 1501–1514 (1959).

² Bird, J. F., Haar, L., Hart, R. W., and McClure, F. T., "Effect of solid propellant compressibility on combustion instability," J. Chem. Phys. **32**, 1423-1429 (1960).

³ Hart, R. W. and Cantrell, R. H., "Amplification and attenuation of sound by burning propellants," AIAA J. 1, 398-404 (1963).

⁴ Horton, M. D. and Rice, D. W., "The effect of compositional variables upon oscillatory combustion of solid rocket propellants," Combust. Flame 8, 21–28 (1964).

⁵ Cantrell, R. H., Hart, R. W., and McClure, F. T., "Linear acoustic gains and losses in solid propellant rocket motors," AIAA J. 2, 1100-1105 (1964).

^{‡‡} This relationship is not immediately obvious from a cursory examination of Eq. (6d). It must be recalled from Ref. 1 that $d\Delta H_v(T_c) = (C_p - C_s)dT_c$.

^{§§} Row 1 of the product matrix is Eq. (A3a); row 2 is the steady-state incremented form of Eq. (2a) when $d\bar{G}_{03}$ is eliminated; row 3 is Eq. (2d); and row 4 is the perturbed form of Eq. (A2).