

A Review of Calculations for Unsteady Burning of a Solid Propellant

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Nomenclature

A	$= A = E(1 - \bar{\tau}_i)$
A_b	$=$ admittance function, Eq. (1)
B	$=$ sensitivity of gas phase to pressure changes
c, c_p	$=$ specific heats of solid and gas
E_s	$=$ activation energy for surface reaction
E	$= E = E_s/RT_s$
h	$=$ enthalpy
H_p	$=$ latent heat for surface reaction; $H_p > 0$ for exothermic surface reaction
H	$= H = H_p/c\bar{T}$
\bar{m}	$=$ average mass flux
m'_s	$=$ fluctuation of mass flux at the surface
n	$=$ index in the linear burning rate law, $r = ap^n$
n_s	$=$ index in the surface pyrolysis law, Eq. (25)
Q_d	$=$ average heat release (per unit volume) in solid
Q'	$=$ heat release in gas phase
$q'_{0\pm}$	$=$ fluctuations of heat transfer at the average position of the surface, $x = 0$
$q'_{s\pm}$	$=$ fluctuations of heat release at the burning surface
r	$=$ linear burning rate
R_0	$=$ universal gas constant
T_i	$=$ initial temperature of propellant, $x \rightarrow -\infty$
T_s	$=$ temperature of burning surface
T_f	$=$ flame temperature
\bar{T}_c	$=$ average chamber temperature, $x \rightarrow +\infty$
x_s, \dot{x}_s	$=$ surface displacement, velocity
$X_{\tau-}, X_{\tau}$	$=$ functions defined in Eqs. (22) and (27)
X_{p-}, X_p	$=$ functions defined in Eqs. (22) and (27)
ϵ	$=$ stands for p'/\bar{p}
λ	$=$ Eqs. (17-20)
λ_p, λ_g	$=$ thermal conductivities of solid and gas
μ	$=$ stands for (m'_s/\bar{m})
ρ_p, ρ	$=$ density of solid propellant and gas phase
$\bar{\rho}_c$	$=$ average density in chamber
τ	$=$ normalized temperature or a time lag
Ω, Ω_g	$=$ dimensionless frequency parameters for the solid and gas phases; Eqs. (18) and following Eq. (34)
ω	$=$ real angular frequency
$(-)$	$=$ mean value
$()'$	$=$ fluctuating value
$()_s$	$=$ evaluated at the solid-gas interface

$()_{s\pm}$	$=$ evaluated on the gas (+) or solid (-) side
$()_{0\pm}$	$=$ evaluated on the gas or solid side of the mean position of the burning surface
$()_f$	$=$ evaluated at the flame, or just downstream of the flame
$()_r$	$=$ real part
$()_i$	$=$ imaginary part

Introduction

THE numerous oscillatory and transient motions that have been found in solid propellant rocket motors share an obvious feature; their existence depends ultimately on some kind of coupling between the motion and combustion. Although it is possible that residual chemical reactions within the gas phase may, under some circumstances, be important, it appears at the present time that they may be ignored. A truly significant interaction occurs principally in a relatively thin region near the burning solid surface. The coupling may be associated, in general, with either changes of pressure or of velocity parallel to the surface. By far, most of the attention given to this problem has been concerned with pressure coupling, and the emphasis of this paper is set accordingly. However, there is evidence that "velocity coupling" may be important in some cases.^{5,6}

Perhaps the simplest problem that requires knowledge of the response of a burning surface is that involving small amplitude acoustic waves. This was the earliest case treated, and hence the term "admittance function," borrowed from acoustics, is commonly used. In the analysis of acoustic waves in a chamber,¹⁻³ it is necessary to specify the component of velocity normal to the boundary. Following traditional acoustics practice, it has usually been assumed that the fluctuation of velocity u' is proportional to the fluctuation of pressure p at the surface; the coefficient of proportionality, in suitably normalized form, is the admittance function A_b for the burning surface. The definition used here is

$$A_b = (u'/\bar{u})/(p'/\gamma\bar{p}) = \bar{M}_b[(u'/\mu)/(p'/\gamma\bar{p})] \quad (1)$$

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where \bar{a} is the average speed of sound, \bar{p} is the mean pressure and γ is the ratio of specific heats. The Mach number and speed of the mean flow leaving the surface are \bar{M}_b and \bar{u} . This is in fact a natural definition so far as the burning process is concerned, since, in response to a pressure change, there is a change in the rate at which solid is converted to gas, and this must appear partly as a velocity fluctuation.

It is generally easier to compute the small change m' of mass flux ($m = \rho u$ where ρ is the gas density) in response to a small change of pressure. Obviously, since $m' = \bar{p}u' + \rho'u$, (1) gives

$$A_b = \bar{M}_b \left[\frac{(m'/\bar{m})}{(p'/\gamma\bar{p})} - \frac{(\rho'/\bar{\rho})}{(p'/\gamma\bar{p})} \right] \quad (2)$$

(\sim) denotes time averaged quantities and ($'$) denotes fluctuations. The bracket is evaluated just downstream of the burning region so that, if one assumes that the oscillations are isentropic, $p \sim \rho^\gamma$, the second term is unity. Further remarks on this point will be offered later. The real part of the first term is often given the symbol $\gamma(\bar{\mu}/\bar{\epsilon})$,

$$\bar{\mu}/\bar{\epsilon} = \text{Re}[(m'/\bar{m})/(p'/\bar{p})] \quad (3)$$

and much of the later discussion will be concerned with $\bar{\mu}/\bar{\epsilon}$ or the entire complex ratio, rather than A_b .

The function A_b is, in general, a complex quantity, depending on the properties of the materials involved as well as frequency. It is helpful to think in terms of harmonic motions and to measure phases with respect to the pressure oscillation. The real part of A_b gives that fraction u' , which is in phase with the pressure. Consequently, the instantaneous rate at which work is done by the surface region on the waves in the chamber is $u'p' = (\gamma\bar{p}/\bar{a})A_b^{(r)}p'^2$, $A_b^{(r)}$ being the real part of A_b . Hence the attenuation, or growth constant for steady waves, has a part proportional to $A_b^{(r)}$ such that the waves are driven if $A_b^{(r)}$ is positive. A larger value of $A_b^{(r)}$ implies a greater tendency for combustion to drive the waves. Although it is a useful relative measure, the admittance function alone is not sufficient to describe the stability of waves in a given chamber; there is a further contribution of comparable magnitude due to interaction between the fluctuating and mean flows at the surface.^{3,4} A valid statement of the stability of waves must be based on a proper accounting of all energy losses and gains.

A similar interpretation of the admittance function arises in connection with the reflection of a traveling wave from a surface. Consider, for example, a plane wave traveling to the left and reflected from a flat surface oriented normal to the direction of propagation. If the interaction between the mean flow and the fluctuations is ignored, then it is quite easy to show that the complex amplitude (i.e., both magnitude and phase are included) of the reflected wave is $(1 + A_b)/(1 - A_b)$ times the amplitude of the incident wave (see Eq. (A7) of Ref. 18).

For the classical acoustic modes, therefore, the velocity fluctuation v' parallel to the surface does not enter in a natural, direct way. However, it may clearly be important because of its possible erosive influence on the burning rate, thereby causing a fluctuation of velocity normal to the surface. A difficulty arises because the surface responds to the magnitude of the total velocity parallel to the surface, which includes the mean flow. Moreover, there may be a threshold to the magnitude of the net velocity, below which the erosive response is essentially zero. The analysis in any case becomes nonlinear.⁵⁷ Since these questions have not been thoroughly treated analytically, and there seems to be limited usable relevant data in the literature, they will not be discussed here.

On the other hand, an increasing amount of experimental information is being obtained for the case of pressure coupling. Unfortunately, systematic interpretation of the data is lagging considerably. One would like to be able, eventually, to classify propellants, at least roughly, according to correlations

between composition and the admittance function. This will probably be accomplished, if at all, only if one understands something of the effects that changes of composition have on the various steps in the unsteady combustion process. Hence, it is clear that analytical work is a necessary guide to interpretation of the experimental work, even though precise quantitative results cannot be expected.

Soon after it had been recognized that the admittance or response function must be known for the study of oscillations in rocket chambers, a laboratory apparatus, the T-burner, was devised⁵⁻⁸ for measuring this quantity without firing a complete rocket. Full usefulness of this technique has not yet been realized, partly because there is not available a thorough analysis of the T-burner itself, which is required for indirect determination of the admittance function from the direct measurement of pressure only. More recently,⁹⁻¹⁴ it has become apparent that a different device, the L*-burner, can also be used to measure the admittance function. Although this provides again an indirect measurement, the analysis used is considerably simpler and probably more accurate. To cover the entire frequency range of interest, both kinds of measurement seem to be necessary. One therefore has a means of experimentally determining a boundary condition required for analytical treatment of waves in a chamber.

The subject of this review is consequently of considerable importance, not only in application to problems encountered in rocket motors, but also for the treatment of laboratory data that should eventually be useful in the design of solid propellant rockets. Calculation of the admittance functions is by no means a closed subject at the present time, and, indeed, it is only now becoming possible (maybe) to extract sufficient information from observations that one may select the "correct" or "valid" analyses. Thus, the comparison of theory and experiment included in the present work is relatively brief.

In a very rough way, the various analyses fall into three categories: time-lag theories, pure heat-transfer theories, and (more or less) "complete" calculations. The first two classes are practically obsolete now, but should be placed in perspective and hence are given more than passing mention. Following a summary of time-lag theories, the complete linearized problem is discussed to exhibit those features which are common to all calculations. The remaining analyses are subsequently discussed within a common structure based on splitting the problem into separate treatments of the solid and gas phases. These are matched through the energy balance at the interface.

The main difference between the calculations lies in apparently distinctive results for the heat transfer from the gas to the solid phases. However, it will be seen that in fact a majority of the results found for the response function have exactly the same form, Eq. (43). This is a consequence of four basic assumptions: 1) one-dimensional analysis of a homogeneous solid phase; 2) no condensed phase reactions; 3) simple pyrolysis of solid to vapor, independent of pressure; 4) quasi-static behavior of gas phase. Failure of one or more of these assumptions is probably the reason that there is quite unacceptable agreement between Eq. (43) and some experimental results.

Much of this work has appeared since Cheng¹⁵ published his useful survey of the subject. Geckler¹⁶ and Schultz et al.¹⁷ have also prepared brief summaries. This review is necessarily terse at certain stages; some of the points are discussed in greater detail in Ref. 18.

Time-Lag Theories

It appears that the earliest published treatment of acoustic oscillations in a solid propellant rocket chamber is that of Grad.¹⁹ Although his analysis of the stability problem is unnecessarily complicated and yields some incorrect quantita-

tive results (particularly the prediction that the most unstable modes are of much higher order than those actually observed), the formulation of the over-all problem is partially similar to those now used. Moreover, he is led naturally to introduce an admittance function in the following way. Suppose that the mass flux leaving the solid (see Fig. 1) is a given function $f(p, T)$ of the pressure and temperature downstream of the burnt gases; $f(p, T) = \rho u$ is the result one would obtain by steady-state measurements. Let m be the actual mass flux under unsteady conditions and assume that the rate of change of m with time is proportional to the difference between the actual mass flux and that which would exist in steady state for the same pressure and temperature:

$$dm/dt = (1/\tau)(f - m) \tag{4}$$

The relaxation time, or time constant, or time lag is τ , and (4) is merely a statement that the burning process tends to return the mass flux to its instantaneous equilibrium value (f). Thus, for a step change of f (due to a change of pressure, say), the mass flux changes as $e^{-t/\tau}$. Both f and m may be represented as sums of mean values (independent of time) and fluctuations: $f = \bar{f} + f'$ and $m = \bar{m} + m'$; in steady burning, $\bar{f} = \bar{m}$.

For harmonic fluctuations having frequency ω , an expression for the mass flux response function is easily found from Eq. (4):

$$(m'/\bar{m})/(p'/\bar{p}) = [b\tau(\bar{p}/\bar{m})]/(1 + i\omega\tau) \tag{5}$$

Grad treats τ and b as independent quantities, neither a function of frequency; b is determined from the dependence of f on pressure and temperature, supposed known. However, if (5) is to correspond to the correct low-frequency behavior of real propellants, b and τ must be related. Usually, the linear burning rate r varies as a power of pressure, $r \sim p^n$. Hence, for a very slow, small change of pressure, $r'/\bar{r} = n(p'/\bar{p})$, and, since $m = \rho_p r$ where ρ_p is the density of the solid,

$$m'/\bar{m} = n(p'/\bar{p}) \quad (\omega \rightarrow 0) \tag{6}$$

in the limit of zero frequency. This limit will be used many times; it amounts to satisfaction of the surface energy balance in steady burning.²⁹ Application of (6) to (5) gives $\tau = n\bar{m}/b\bar{p}$, and (5) becomes

$$(m'/\bar{m})/(p'/\bar{p}) = n/(1 + i\omega\tau) \tag{7}$$

Typical numerical values lead to $\tau \approx 10^{-5}$ sec. It is perhaps useful to exhibit τ explicitly as a time lag by rewriting (7) as

$$\frac{m'}{\bar{m}} = \frac{p'}{\bar{p}} \frac{n(1 - i\omega\tau)}{1 + \omega^2\tau^2} = \frac{n\bar{\epsilon}}{(1 + \omega^2\tau^2)^{1/2}} e^{i\omega(t-\tau)} \tag{8}$$

where $\bar{\epsilon}$ is the amplitude of the pressure oscillation. More to the point, however, is the behavior of (7) as a function of frequency. The real part is $n/(1 + \omega^2\tau^2)$ which starts at n for $\omega = 0$ and vanishes as $\omega \rightarrow \infty$. All measurements that have been reported show a definite peak in $\bar{\mu}/\bar{\epsilon}$ at some moderate frequency, generally less than a few thousand cycles per second. Hence, this very simple picture, perhaps the most elementary one can devise, is wholly inadequate to describe the interaction between pressure waves and the burning. The essential reason for the failure is that the "time lag" τ is in fact a very strong function of frequency which, in the more detailed computations discussed later, can apparently be determined to a rather good approximation for some cases.

Much more extensive work was done by Cheng^{15,20-24} using the idea of a time lag, although defined quite differently from Grad's response time. The formulation was in this case strongly influenced by, and is quite similar to, the extensive development of the time lag for analysis of instabilities in liquid propellant rocket motors.²⁵⁻²⁷ For a given amount of propellant, τ is now the time lag between the

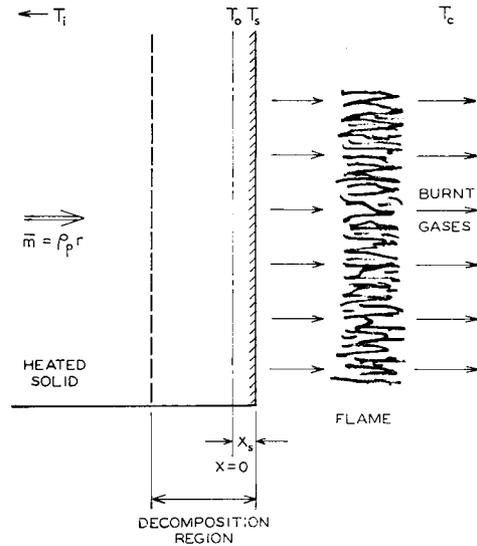


Fig. 1 Sketch of the model used.

moment of pyrolysis at the surface and combustion in the homogeneous flame region. Let $m_s(t - \tau)$ denote the instantaneous mass flux at the surface, so that $m_s(t - \tau)d(t - \tau)$ grams of solid are converted to gas in the interval $d(t - \tau)$ at time $t - \tau$; this later burns in the interval dt at the time t and at the rate $m(t)$, the same mass flux appearing in the definition of the admittance function. Thus, the conservation of mass implies

$$m(t) = [1 + (d\tau/dt)]m_s(t - \tau) \tag{9}$$

Now the essential assumption is made that, before burning (i.e., in the interval τ), the propellant absorbs a fixed amount of energy and that this is related to the pressure according to

$$\int_{t-\tau}^t p^\nu(t')dt' = \text{const}$$

It may be noted, as later remarks will amplify, that, in all computations of the admittance function, the pressure may be assumed uniform, through varying in time, in both the solid and gas phases. The further assumption is made that the instantaneous surface mass flux is related to the instantaneous pressure, with no phase or time lag, according to

$$m_s(t - \tau) = \text{const} [p(t - \tau)]^n = (\bar{m}/\bar{p}^n) [p(t - \tau)]^n$$

the second equality following in order to satisfy the condition that in steady burning $m_s = \bar{m}$, and of course $p = \bar{p}$ at all times. (Cheng¹⁵ also includes dependence on erosion, but that will be ignored here.) Suitable combination of the preceding equations gives

$$m(t)/\bar{m} = (1/\bar{p}^n) \{ p^\nu(t)/[p(t - \tau)]^{\nu-n} \} \tag{10}$$

which is Eq. (5) of Ref. 20. Roughly, then, n is interpreted as the index in the linear burning rate law $r \sim p^n$ and ν is an index associated with the gas phase reactions.

As before, a relation between m' and p' can be found; for harmonic fluctuations,

$$\frac{m'/\bar{m}}{p'/\bar{p}} = \nu - (\nu - n)e^{-i\omega\tau} = \left(n \left/ \left\{ 1 + \frac{(\nu - n)[-1 + e^{-i\omega\tau}]}{\nu - (\nu - n)e^{-i\omega\tau}} \right\} \right) \tag{11}$$

Note that for $\omega \rightarrow 0$, (11) tends to the correct limit if n is interpreted as suggested previously. Comparison of (11) and (7) shows that the time lags defined by Grad and Cheng are not related in a particularly simple way.

The real part of (11) is

$$\bar{\mu}/\bar{\epsilon} = \nu - (\nu - n) \cos(\omega\tau) \tag{12}$$

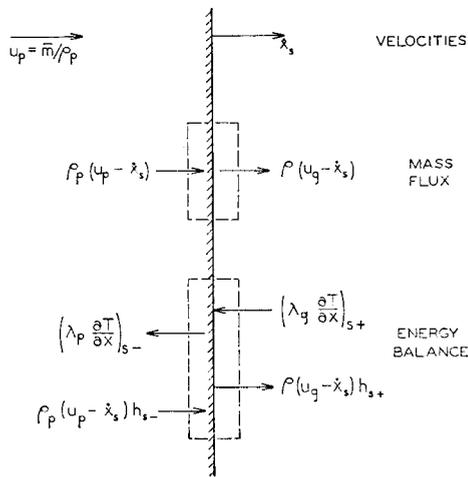


Fig. 2 Control volumes for the interface conditions.

As a function of frequency, for fixed τ (again assumed to be independent of frequency), (12) exhibits infinitely many peaks. Figures 2-4 of Ref. 15 show some numerical results computed by Cheng. By proper choice of ν and by letting τ vary with frequency (Cheng chooses $\tau \sim \omega^{-2/3}$), it is possible to force only a single peak. This is clearly an unsatisfactory situation; one is merely fitting a curve and is not in a position to predict results or to interpret given results in any detail, a short-coming thoroughly recognized by Cheng.

The result (11) was used in studies of the stability of waves in chambers²⁰⁻²³ for various configurations and types of propellants. However, statements about stability depend rather strongly on the shape of the admittance function (or $\tilde{\mu}/\tilde{\epsilon}$) as a function of frequency. Hence, conclusions based on formulas such as (7) or (11) are suspect.

As in the case of Grad's computation, the representation in terms of a time lag is evidently oversimplified. One gain,¹⁹ however, is that (11) does not vanish as $n \rightarrow 0$, whereas (7) does. Even if $n = 0$, so that the burning rate is insensitive to pressure changes in the low-frequency limit, there is no reason to expect a similar result at high frequencies. More detailed analyses support this contention.

Moore and Maslen²⁷ also introduced a time lag in their discussion of the stability of waves. Their final result, expressed in their Eq. (16) for the growth constant, shows that their assumptions are equivalent to the statement that the admittance function is a complex number.

In terms of the magnitude and phase ϕ of A_b , $A_b = |A_b| \exp(-i\phi)$, a time lag τ can be defined as $\omega\tau = -\phi$. According to the definition (1), τ evidently represents the lag between pressure and velocity fluctuations. A more direct comparison with Eqs. (7) and (11) can be made by solving (2)

for $(m'/\bar{m})/(p'/\bar{p})$ to give

$$\frac{m'/\bar{m}}{p'/\bar{p}} = \left(n \left/ \left\{ 1 + \frac{[(\gamma n - 1) - \bar{M}_b^{-1}|A_b|e^{-i\omega\tau}]}{[1 + \bar{M}_b^{-1}|A_b|e^{-i\omega\tau}]} \right\} \right) \quad (13)$$

The low-frequency limiting condition has been applied; at $\omega = 0$, when $A_b = A_{b0}$, the condition implies $A_b^0 = \bar{M}_b(\gamma n - 1)$. In fact, (13) is not especially useful or enlightening; the only point is that, so far as the relation between velocity and pressure fluctuations at the surface is concerned, the natural time lag is defined in terms of the real and imaginary parts of the admittance function.

It appears that Moore and Maslen used a definition of τ like that of Eq. (13). However, it was introduced arbitrarily, following quite a different approach, and they had no way of computing or estimating it. Once again, τ is a strong function of frequency as well as the properties of the propellant.

Three distinct definitions of a time lag have been discussed in this section; more will arise shortly. They all suffer from the inevitable weaknesses of any ad hoc hypothesis: that they are known only by a more detailed analysis (in which case they become trivial definitions) or they must be measured. If a time lag is used in a complete analysis of waves in a chamber, then an inverse problem must be solved: if all other quantities are known, what values of τ (and perhaps additional parameters) lead to unstable waves? This has been a reasonably successful approach for liquid rockets (Ref. 25, for example,) principally, it seems, because the time lag is at most a very slow function of frequency; the dependence on combustion parameters (fuel/oxidizer ratio particularly) may be inferred from observation of the stability boundary. This happens to be a fortunate situation, since there exists no way of computing τ for a liquid rocket. On the other hand, the situation in a solid propellant rocket is just reversed; although τ is a function of frequency (and therefore geometry and mode), it may, possibly, not only be measured but calculated.

Formulation of the More Complete Problem

Although it is easy to classify those analyses which rely heavily on some sort of arbitrary time lag, there is a great deal of overlap among the remaining treatments—in fact, much more than one would gather from a brief perusal. It therefore seems advisable to construct at this stage a rather broad description of the problem, providing a reference framework. There is fairly obvious and general agreement concerning the gross aspects of the combustion process: cold solid is heated, perhaps decomposes in a region near the solid-gas interface, vaporizes (the "pyrolysis" reaction), and burns in the gas phase. These features are sketched in Fig. 1. Naturally, there are many more details which must be accounted for: differences between composite and double-base propellants, burning of metallic particles, influence of ballistic additives, inhomogeneities of the various regions, and the

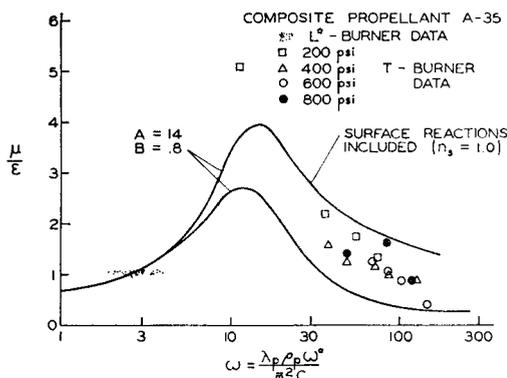


Fig. 3 Comparison of Eqs. (43) and (51) with some experimental results for a composite propellant (A-35).⁵⁴

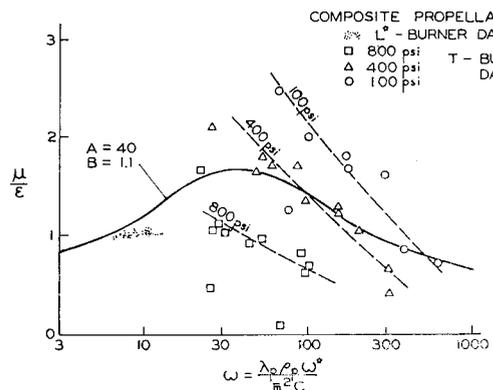


Fig. 4. Comparison of Eq. (43) with some experimental results for a composite propellant (A-13).⁵⁴

complicated character of the gas phase. Some of these will be treated subsequently; some have yet to be studied adequately.

It happens, however, that all calculations with which the author is acquainted may be treated as "three-region" the solid phase, the gas phase, and the interface region. The last is generally collapsed to a plane and provides a very important matching condition between the solid and gas phases. Except for one recent calculation, the solid has been treated as a single homogeneous layer up to the interface, and there is virtual unanimity on the solution for the condensed phase. Hence, the analyses differ importantly only in regard to handling the gas phase.

The problem will be analyzed in one-dimensional form, and, unless otherwise specified, all material properties are averaged over the chemical composition. Three-dimensional properties, such as those necessarily present in the composite propellants, are therefore hidden; at present, there is no way of treating such complications, and the problem may perhaps best be regarded as one of determining the appropriate averaging procedure. There are several attempts to approximate the difference between composite and double-base (i.e., homogeneous) propellants, but inhomogeneities in the interface and the influence of metal particles have not been studied.

During unsteady burning the interface moves relative to its mean position; when the pressure oscillates harmonically, the surface does so as well. In all but two works,^{28,29} a coordinate system attached always to the burning surface is used; this is not an inertial system. The author prefers an inertial system, with origin fixed to the average position of the burning surface, which moves at rate r in the laboratory. This system, which is similar to the choice made in thin airfoil theory, was first used in this problem by Williams;²⁸ the equivalence of results obtained in the two systems is easily demonstrated.¹⁸ Thus, in Fig. 1, the solid appears to be moving from the left at the steady linear burning rate r . Since the actual burning surface oscillates about the origin, some care must be taken with the boundary conditions.

Solid Phase

Because the conservation of mass and momentum is trivially satisfied, the energy equation alone, written for the temperature, needs to be considered in the solid phase:

$$\lambda_p(\partial^2 T/\partial x^2) - \bar{m}c(\partial T/\partial x) - \rho_p c(\partial T/\partial t) = -\dot{Q}_d \quad (14)$$

where \dot{Q}_d is the rate of generation of heat per unit volume accompanying decomposition. Only in Ref. 29 is \dot{Q}_d taken to be nonzero in a finite region, so for simplicity here only the case $\dot{Q}_d = 0$ will be treated in a detailed manner. With dimensionless variables, $\tau = T/\bar{T}_s$, $\xi_p = mcx/\lambda_p$, (14) is

$$(\partial^2 \tau/\partial \xi_p^2) - (\partial \tau/\partial \xi_p) - (\lambda_p \rho_p/\bar{m}^2 c)(\partial \tau/\partial t) = 0 \quad (15)$$

The normalized mean temperature is

$$\tau = \tau_i + (1 - \tau_i)e^{\xi_p} \quad (16)$$

meeting the conditions $T = \bar{T}_s$ at the surface and $T = T_i$ far downstream in the cold propellant.

For harmonic motions $\tau' \sim \exp(i\omega t)$, the spatial dependence is easily determined from (15) to be $\exp(\lambda \xi_p)$; λ satisfies the equation

$$\lambda(\lambda - 1) = i\Omega \quad (17)$$

where Ω now stands for the important dimensionless frequency parameter

$$\Omega = \lambda_p \rho_p \omega/\bar{m}^2 c \quad (18)$$

In order that $\tau' \rightarrow 0$ for $x \rightarrow -\infty$, the solution of (17) with positive real part must be used; $\lambda = \lambda_r + i\lambda_i$, and

$$\lambda_r = \frac{1}{2}\{1 + [1/(2)\Omega^2][(1 + 16\Omega^2)^{1/2} + 1]^{1/2}\} \quad (19)$$

$$\lambda_i = [1/2(2)\Omega^2][(1 + 16\Omega^2)^{1/2} - 1]^{1/2} \quad (20)$$

It will be apparent shortly that what one really needs is a formula for the fluctuation of heat transferred from the solid-gas interface to the solid; in dimensionless form this is $q'_{s-} = (\lambda_p/\bar{m}c\bar{T}_s)(\partial T'/\partial x)'_{s-}$. When the motion and vaporization of the surface are properly accounted for, the result is (e.g., Appendix B of Ref. 18):

$$q'_{s-} = [\lambda + (A/\lambda)e^{-i\omega\tau_1}]\tau'_{s-} + (n_s/\lambda)e^{-i\omega\tau_2}(p'/\bar{p}) \quad (21)$$

where $A = E_s(1 - \tau_i)/R_0\bar{T}_s$ contains the activation energy associated with surface pyrolysis. The time lags τ_1 , τ_2 are defined in Eq. (26). If a decomposition region of finite thickness within the solid phase is included, then q'_{s-} has the form,²⁹

$$q'_{s-} = X_{\tau-}\tau'_{s-} + X_{p-}(p'/\bar{p}) \quad (22)$$

but the coefficients of τ'_{s-} and p'/\bar{p} are considerably more complicated.

Solid-Gas Interfacial Region

Conservation of mass and energy and the law for conversion of solid to gas give three important relations. The first two are easily found by considering a small control volume placed about the true burning surface which is located at $x = x_s$ and moves with speed \dot{x}_s .²⁹ Thus, if the region can be collapsed so that negligible amounts of mass and energy are continued within it, one finds "jump" conditions associated with total unsteady mass and energy transfer on the upstream ($s+$) and downstream ($s-$) sides:

$$\rho_p \dot{x}_s/\bar{m} = -[1 - (\bar{p}/\rho_p)](m'_{s-}/\bar{m}) \approx -(m'_{s-}/\bar{m}) \quad (23)$$

$$[\lambda_p(\partial T'/\partial x)]_{s+} = [\lambda_p(\partial T'/\partial x)]_{s-} + \bar{m}[1 - (\rho_p \dot{x}_s/\bar{m})](-H_p) \quad (24)$$

The mean gas density \bar{p} near the surface is always much smaller than the solid density in the cases of current interest, so the term \bar{p}/ρ_p will hereafter be dropped. The enthalpy change $H_p = h_{s-} - h_{s+}$ accompanying the surface reaction is positive for an exothermic reaction; note that $[\lambda_p(\partial T'/\partial x)]_{s-}$ is the heat flux from the interface to the solid, and $[\lambda_p(\partial T'/\partial x)]_{s+}$ is the heat flux to the interface from the gas phase.

Usually, an Arrhenius law has been assumed for the conversion of solid to gas, giving the total surface mass flux

$$m_s = B\bar{p}^{n_s}e^{-E_s/R_0T_s} \quad (25)$$

In most cases, the dependence on pressure has been ignored ($n_s = 0$). A general perturbed form of (25), to first order of small quantities, is

$$m'_{s-}/\bar{m} = Ee^{-i\omega\tau_1}\tau'_{s-} + n_s e^{-i\omega\tau_2}(p'/\bar{p}) \quad (26)$$

with $E = E_s/R_0T_s$ the dimensionless activation energy for the surface reaction. The time lags τ_1 , τ_2 are arbitrarily introduced to represent the lag (or lead) between the fluctuations of surface temperature and pressure, and the corresponding contributions to the fluctuation of surface mass flux. At the present time, there is no way of computing them on the basis of known chemical kinetics. Hence, they will be ignored for the most part, but they have been included as unknown parameters in several of the works discussed later.

So far as a linearized problem is concerned, the assumption of an Arrhenius law (25) has little significance. What matters is the statement that the surface mass flux responds to be surface temperature and pressure changes; the linear relation (26) must then hold. If one chooses to deduce (26) from (25), then this merely provides a familiar interpretation of the parameters E and n_s . Incidentally, the use of (26) is not universal; in some of the work of McClure and co-workers, it was assumed that the mass flux was sensitive to heat-transfer fluctuations [see Eq. (37)].

In some way, all calculations must involve the aforementioned conditions, although perhaps in slightly modified forms which will be noted as required. Since the various studies differ mainly in respect to the treatment of the gas phase, it seems best to use the linearized form of (24) as the pivotal matching condition. If, in addition, (26) is assumed, one has

$$(c_p/c)q'_{s+} = q'_{s-} + X_\tau \tau'_s + X_p(p'/\bar{p}) \quad (27)$$

where

$$X_\tau = (c_p/c) - 1 - EHe^{-i\omega\tau} \quad (28)^*$$

$$X_p = -n_s \bar{H} e^{-i\omega\tau^2} \quad (29)$$

The right-hand side of (27) is the formula for q'_{s+} which accounts for the behavior of the solid phase and conservation of energy at the interface. Once q'_{s+} provided by the gas phase has been determined by solution of the gas phase problem, then the analysis is effectively complete, for then (27) will give $\tau'_s/(p'/\bar{p})$, and $(m'_s/\bar{m})/(p'/\bar{p})$ can be found from (26). Solution of the problem in the gas phase will also provide a relation between m'_s and the value of m' at the downstream boundary required in the admittance function, Eq. (2). For subsequent use, the normalized form of the mean energy balance at the surface is obtained from (24) and (16):

$$(c_p/c)\bar{q}_{s+} = \bar{q}_{s-} - H = 1 - \tau_i - H \quad (30)$$

Gas Phase

This is by far the most involved part of the problem; not only are the equations more difficult to handle, but it is not clear what approximations are appropriate for which propellants. Thus, practically, the limited success achieved to the present time has been gained with the simplest analyses. An essential reason for this is that much of the behavior in the frequency range of interest is evidently dominated by the response of the solid phase, and it appears that the straightforward solution leading to (21) is adequate. Hence, the gas phase can be simplified considerably without destroying certain major features of the problem. It remains to be seen just how simple yet representative it can be, but there are indications that some results are oversimplified.

If diffusion of the separate species is accounted for, familiar forms for the conservation equations of mass, concentration, and energy are

$$(\partial\rho/\partial t) + (\partial m/\partial x) = 0 \quad (31)$$

$$\rho(\partial k_i/\partial t) + \rho u(\partial k_i/\partial x) - (\partial/\partial x)[\rho D(\partial k_i/\partial x)] = \omega_i \quad (32)$$

$$\rho \frac{\partial h}{\partial t} + \rho u \frac{\partial h}{\partial x} = \frac{\partial}{\partial x} \left(\frac{\lambda_g}{c_p} \frac{\partial h}{\partial x} \right) + \frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left[\frac{\lambda_g}{c_p} (Le - 1) \Sigma h_i \frac{\partial k_i}{\partial t} \right] \quad (33)$$

where the enthalpy for each species is h_i and $h = \Sigma k_i h_i$. The only calculations^{28,30,31} including diffusion explicitly do so for Lewis number Le equal to unity, in which case the energy equation (50) can be written

$$\frac{\partial}{\partial x} \left(\lambda_g \frac{\partial T}{\partial x} \right) - mc_p \frac{\partial T}{\partial x} - \rho c_p \frac{\partial T}{\partial t} = -\dot{Q} - \frac{\partial p}{\partial t} \quad (34)$$

The local rate at which heat is released per unit volume is \dot{Q} .

The equation for conservation of momentum reduces to the statement that the pressure is approximately uniform throughout the region treated, but varies with time. This is a consequence of the low speeds and long wavelengths involved; a closer estimate may be found in Ref. 28, p. 3160.

Apart from the obvious complications if diffusion is accounted for, the truly serious obstacle to solving the equations for the gas phase is that in general (31) and (33) or (34)

are coupled through the density in $\partial\rho/\partial t$. The simplest and usual means of avoiding the difficulty is to assume that the frequency is sufficiently "small" that all time derivatives in the gas phase can be ignored; this is the quasi-static or low-frequency approximation and (31) gives simply $m \approx m_s$. For example, if (33) is written in terms of dimensionless variables with $\xi_g = mc_p x/\lambda_g$ corresponding to ξ_p in the solid phase, then the frequency parameter for harmonic oscillations is $\Omega_g = \lambda_g \rho_c \omega/\bar{m}^2 c_p$. That is, the terms involving time derivatives in (31-33) contain Ω_g as a factor and are assumed negligible for $\Omega_g \ll 1$. Some representative properties are shown in the list of symbols; with those values and $\bar{p} < 100$ atmospheres, $\Omega_g < \omega/100$. Also, however, $\omega \approx f/40r^2$ where f is the frequency (cps) and r is the linear burning rate (cm/sec). For $r = 1$ cm/sec and $f < 1000$ cm/sec, Ω_g is small but certainly not negligible. See Ref. 1 for further comments on this point.

The ratio Ω_g/Ω is effectively a measure of the ratio of the thermal response time in the gas to that in the solid; the gas responds more quickly because, owing to a lower density, the volumetric heat capacity is much smaller. Since for many (but certainly not all) chemical reactions the response time is also much less than the thermal response time for the solid phase, one might expect the quasi-static approximation to be fairly good under some conditions. Brief discussions of this simplification will also be found in some of the references (e.g., 1, 28-30, 32). Bird, et al.³² found that for their treatment of the gas phase the approximation seems to be quite good up to 10^4 cps. The accuracy of the approximation cannot be verified without having more elaborate solutions, but the only work in which the assumption of quasi-static behavior is not eventually made is Ref. 1. Experimental results cited later suggest that the assumption may fail at frequencies lower than one would expect on the basis of crude estimates.

Practically all of the following discussion will not involve explicit time derivatives in the gas phase. This means that expressions found for q'_{s+} required in Eq. (27) will be independent of frequency. Hence, variations of m'_s and the admittance function with frequency will be solely consequences of the relatively slow response of the solid, i.e., due to the propagation of thermal waves inward from the solid-gas interface.

Intermediate Theories

As formulated here and, indeed, as treated in the literature, the problem reduces principally to computation of q'_{s+} , the fluctuation of heat transfer from the gas phase in the interface. Except for those labelled earlier as time-lag theories, all of the computations focus essentially on heat transfer and are perhaps justly called "thermal theories" in the sense that, whatever might be claimed at the beginning of an analysis, diffusion of mass eventually winds up very much in a minor position. However, the calculations covered in this section fall, in a more or less loose sense, somewhere between the time lag theories and those treated later as the most complete calculations available.

Some of these involve fluctuations of velocity parallel to the surface so that they are, in effect, concerned with velocity coupling rather than pressure coupling. However, they are not concerned with the nonlinear aspects of velocity coupling which, as noted earlier, seems to be the distinctive features of that problem. Moreover, certain questions such as "self-excited" oscillations were first raised by them.

In particular, two papers by Green³³ and Nachbar and Green³⁴ generated interest.^{15,17,35,36} The relevant part of Green's³³ work consists first in the assumption of an Arrhenius law [Eq. (26)] here, with $n_s = 0$ but non-zero time lag (τ_i) between mass flux and surface temperature fluctuations. The total heat transfer to the surface [Green's Eq. (1)] is assumed to be expressed in terms of a film thickness δ or heat-transfer coefficient h , $q_{s+} = (\lambda_g/\delta)(T_f - T_s) = h(T_f - T_s)$ in

* The fluctuation of H_p is $H'_p = (c - c_p)T'_s$.

dimensional form, with T_f the flame temperature. The argument is then offered that the film thickness must increase if the mass flux from the surface increases; thus h is assumed to have the form $h = F/r$ where F is an unknown factor, roughly expressed as $F = \lambda_0 \rho v / \rho_p l$, l being the distance from the downstream stagnation point in a rocket chamber (i.e., the distance for development of a boundary layer) and v being the velocity parallel to the burning surface.

Green assumes that $F = \bar{F} + F'$ may fluctuate as a consequence of fluctuations of the local velocity parallel to the surface, but the flame temperature is assumed constant. The principal results of the analysis is then the formula for q'_{s+} , which, when combined with the pyrolysis law, the matching condition (22), and $c_p = c$, gives his result¹⁸

$$\tau'_s = \frac{(\tau_f - 1)F'/\bar{m}c\bar{r}}{\lambda + (A/\lambda)e^{-i\omega\tau_1} + (F'/\bar{m}c\bar{r}) + E(1 - \tau_i - 2H)e^{-i\omega\tau_1}} \quad (35)$$

from which m'_s/m can be found. For large ω , $\tau'_s (= \Delta T_s/\tau_s$ in his notation) appears as Eq (20) of Ref. 33, and for ω unrestricted it appears as Eq. (13) of Ref. 34.

Green and Nachbar sought conditions under which the denominator of (35) vanishes, and identified this with the occurrence of "resonance," presumably by analogy with the behavior of a simple second-order system. If all other quantities are fixed, the condition, if it can be satisfied, gives particular values ("eigenvalues") of the frequency ω ; actually, they choose to permit both the frequency and time lag τ_1 to vary and sought the critical values for zeros of the denominator. Since then τ'_s and hence the mass flux change becomes infinitely large even for vanishingly small values of the "driving force" (F'), it was supposed that this condition corresponds to the existence of pressure oscillations (resonant burning) leading to observable increases in the burning rate and mean chamber pressure. It is now recognized that this is a very narrow view of the problem to be discussed in the section on self-excited or "intrinsic" instabilities; oscillations may very well occur even if the denominator is not zero, or even near zero.

For the sake of comparison with later work, it should be remarked that for $\tau_1 = 0$, Eq. (35) leads to a formula for m'_s/m which is, apart from p' replaced by F' , identical with that produced by other calculations. This is shown in Table 1. The analysis by Green and Nachbar of the zeros of the denominator is then exactly the same as the computation by

Denison and Baum³⁰ for the conditions under which self-excited motions arise. A non-zero value of τ_1 modifies quantitative results but is not an essential feature.

The preceding calculation has yielded no quantitative results either for the response function or for the stability of waves in a chamber. Mainly this is a consequence of preoccupation with the very special aspect of intrinsic instabilities which were first noted by Green. Barrère and Bernard³⁷ tried to generalize the computation by introducing additional time lags and also by permitting a continuous distribution of time lags. Their hope was to find a means of representing the behavior of composite propellants, a problem which remains unsolved. A slightly later consideration of the same problem³⁸ also makes use of a time lag, but defines it differently.

Akiba and Tanno⁹ proposed a modification to Green's analysis for use in their experimental study of low-frequency (also called L^* or "nonacoustic") instability. Two important changes were made: 1) the phase lag $\omega\tau_1$ is set equal to zero because of the low frequencies involved and 2) the heat transfer from the gas phase to the solid-gas interface [their Eq. (8)] is written in terms of a pressure-dependent heat-transfer coefficient $h = kp^n$, where k is a constant and n is again the index in the linear burning rate law. (In their notation, the index is $n/2$ and $k = k_0/L$ for $r = bp^n$.) The flame temperature is again taken to be fixed. After the normalized fluctuation of heat transfer is used in the energy matching condition (27), with $X_{p-} = X_p = 0$ and m'_s/m related to τ'_s by (26) with $\tau_1 = n_s = 0$, one finds easily

$$\frac{m'_s/\bar{m}}{p'/\bar{p}} = \frac{nk\bar{p}^{n+1}E/\bar{m}c}{\lambda + (A/\lambda) + X_\tau + (kp^n/\bar{m}c)} \quad (36)$$

Application of the limiting condition for $\omega \rightarrow 0$ eliminates X_τ and yields the two-parameter form shown in Table 1; see also Eq. (43). Sehgal and Strand¹¹ based their discussion on ideas introduced by Akiba and Tanno; neither paper contains explicitly the two-parameter formula for the response function, although it is of course implied.

This response function involves an unsatisfactory assumption for the heat-transfer coefficient, thereby introducing pressure coupling rather than the velocity coupling proposed by Green. The form of the response function is exactly that found by later works (B and A being adjustable parameters independent of frequency), but the basis of the calculations and hence the interpretations of B will be more convincing than in the case just discussed.

Table 1 Summary of response functions with the quasi-static approximation for the gas phase

Reference	$[(m'/\bar{m})/n(p'/\bar{p})]$	Equation no.	Meaning
33	$\frac{E(\bar{\tau}_f - 1)F'}{n\bar{m}c\bar{r}} \frac{F'}{(p'/\bar{p})}$	(63) of Ref. 18	F' : Eq. (58) of Ref. 18 B : Eq. (64) of Ref. 18 $A = E(1 - \bar{\tau}_i)$
9	$\frac{AB}{\lambda + (A/\lambda) - (1 + A) + AB}$	(68) of Ref. 18	$B = \frac{Ekp^{n+1}(\bar{\tau}_f - 1)}{\bar{m}c(1 - \bar{\tau}_i)}$
1, 32	$\frac{AB}{\lambda + (A/\lambda) - (1 + A) + AB}$	(43)	$B = \frac{\bar{\tau}_i}{j(1 - \bar{\tau}_i)}$
42	$\frac{AB + (n_s/n)(\lambda - 1)}{\lambda + (A/\lambda) - (1 + A) + AB}$	(51)	$B = \bar{\tau}_i/j(1 - \bar{\tau}_i)$ $\bar{\tau}_i = T_i/\bar{T}_s$
30	$\frac{AB}{\lambda + \frac{A}{\lambda} - (1 + A) + AB}$	(43)	$B = \alpha$ $\alpha = (c_p/c)/[(1 - \bar{\tau}_i)\epsilon]$ $\epsilon = (\bar{T}_s/\bar{T}_f)[n + 1 + (E_f/2R_0\bar{T}_f)]$
47	$\frac{A(B - \theta_s/A)}{\lambda + (A/\lambda) - (1 + A) + A(B - \theta_s/A)}$	[(53) also Eq. (108) of Ref. 18]	θ_s : after Eq. (53)
52	$\frac{AB}{\lambda + (A/\lambda) - (1 + A) + AB}$	(125) of Ref. 18	$B = 1 + [(c_p/c) - EH]/A$ (Ref. 52) $= 2[1 - H(E/A)] + (1/E)$ (Ref. 49)
49	$\frac{P_1}{X_{\tau-} - X_{\tau+0} + [P_1/(1 - n_s/n)]} + \frac{n_s}{n}$		See Table V of Ref. 18 (This reduces to Eq. (43) for no decomposition and $n_s = 0$.)

Another calculation concerned with intrinsic instabilities rather than the complete response function is the work of Shinnar and Dishon,³⁷ who did not produce any numerical results. They reduce the problem eventually to a calculation of characteristic values which corresponds to determining the zeros of the denominator noted previously. The formulation, however, is incorrect and will not be discussed here (see Ref. 18 for a more complete criticism).

Finally, there are two other works^{37,38} that are sometimes referred to but are now rendered wholly obsolete by more recent work. Smith and Sprenger,³⁹ in a paper which contains one of the first experimental verifications that increases in mean chamber pressure often accompany oscillations, suggested that the coupling was due to the influence of pressure changes on heat release in the gas phase. However, they ignored the important role of heat transfer in the solid phase and assumed that the surface recedes at uniform speed. No calculations were carried out. Smith⁴⁰ assumes that the surface temperature is constant and that the heat transfer from the gas phase (q'_{s+}) is in phase with the pressure oscillations. Both of these approximations are unacceptable, and the subsequent computations are bound to be seriously in error.

More Complete Calculations

The remaining analyses covered here are characterized by more concern with the structure of the flame in the gas phase, and in some instances chemical reactions in the vicinity of the solid-gas interface are considered. So far as the flame is concerned, only the very simplest representations have been used. Several works are based essentially on a planar "flame-front" model, and, in those cases where distributed combustion has been considered, rather severe approximations have been used. It will be seen that the same two-parameter form of the response function is found, no matter what assumptions are made in respect to the detailed structure of the flame. The results can be distinguished only by different formulas for the parameter B . However, if the assumption of quasi-static behavior is relaxed or if the equations are not linearized, then differences in the models for the gas phase flame will affect the response function significantly.

Since publication of the work of Hart and McClure,¹ more emphasis has, properly, been placed on computing the admittance functions and its variation with frequency rather than simply a concern with its poles. Reference 1 is the first attempt to treat the entire process from the viewpoint described here and contains also the only calculation (albeit for a simplified model) of the gas phase valid for frequencies outside the quasi-static range.

There is an important difference in the pyrolysis law used in Ref. 1 leading to a dependence of mass flux on heat transfer rather than on pressure only. In the notion used here, Eq. (36) of Ref. 1 is

$$m'_{s+}/\bar{m} = E\tau'_{s+} + \alpha(q'_{s+}/\bar{q}_{s+}) \quad (37)$$

with α found to be -1 . This result is based initially on the assumption that the solid material decomposes internally at a rate given by the Arrhenius law and that the conversion of solid to gas is the integrated result of the decomposition. One might expect that the mass flux could, under some conditions, be related to the heat transfer, but (37) shows the peculiar (and unexplained in the references cited) result that the mass flux decreases, if $\alpha = -1$, with an increase of heat transfer. However, other features of the calculation mask this difficulty and will be more important.

References 1, 32, 41, and 42 will be considered together, although the last represents somewhat of a break from the earlier three; it does not involve the direct dependence of m'_{s+} on q'_{s+} (i.e., $\alpha = 0$). Very few details will be included; the coverage in Ref. 18 is somewhat more extensive and con-

tains a table showing the correspondence for the more important symbols used.

The solution for the solid phase is the same as that quoted previously, in the form

$$q'_{s-} = \lambda\tau'_{s-} + [(1 - \bar{\tau}_i)/\lambda](m'_{s-}/\bar{m}) \quad (38)$$

This may be extracted from the last equation of the Appendix of Ref. 1, but it should be noted that the equation there is for the total heat transfer, $\bar{q}_{s+} + q'_{s-}$.

The gas phase in Refs. 1, 32, 41, and 42 is based on the assumption of a flame front or slightly modified forms. A boundary condition is set at the downstream edge of the flame region (which is effectively collapsed to a plane) so that the conservation equations are solved without heat release included except as it affects the boundary condition at $T = T_f$; diffusion is also ignored. In Ref. 1, the coupled continuity and energy equations (with $\dot{Q} = 0$) are solved by transforming the independent variables from (x, t) to (T, t) without the strict quasi-static assumption. The dependent variable $\Phi(T, t)$ is essentially the perturbation of $p^{1/\gamma}x$ where x is the position at which the temperature is T and time t . Motion of the flame relative to the burning surface is accounted for and leads to a relatively involved boundary condition there. Eventually, the continuity and energy equations can be combined to give a single second-order equation for Υ [Eq. (20) of Ref. 1], but at the expense of losing interpretation of the formal analysis. From the solution $\Phi(T, t)$ the fluctuation of mass transfer can be found by use of the continuity equation and boundary conditions.

It is perhaps useful to note that a quantity J appears in all four papers; it arises first in Eq. (6a) of Ref. 1, which is a formula for the total heat transfer from the gas phase to the solid. It can be shown¹⁸ that the formula for J is

$$J/c\bar{T}_s = [(q'_{s-} - \tau'_{s-})/(m'_{s-}/\bar{m})] - (1 - \tau_i) \quad (39)$$

in which τ' is found by combining the pyrolysis law and the perturbed part of the energy matching condition. In the special case $\alpha = 0$,

$$J/c\bar{T}_s = (1/E)\{\lambda + (A/\lambda)\} - (1 + A) \quad (40)$$

Although the quasi-static assumption is not made in the differential equations, an "adiabatic" approximation is used to determine formulas for fluctuations in the burning rate both for the pyrolysis law and for the burning rate in the gas phase [cf. Eq. (7) and following remarks of Ref. 1]. In this way, a comprehensive treatment of the flame region is avoided. It appears, however, that this approximation, reducing the flame to a plane surface, may be very restrictive and probably not at all applicable to composite propellants.

The formula for $\bar{\mu}/\bar{\epsilon}$ is lengthy and will not be reproduced here. Evidently, numerical calculations were carried out for much wider ranges of parameters than reported in Ref. 7, for the existence of large peaks (i.e., zeros of the denominator as discussed in connection with Green's work) was noted. However, the numerical results actually given exhibit only broad, rather low peaks. The values of E (34-42) are rather high; more reasonable values are 10-15, that is, $E_s = 20-30$ k cal/mole. The failure to obtain higher peaks, closer to observed results, with acceptable values of the parameters led subsequently to inclusion of thermal radiation⁴¹ and the dependence of the surface reaction on pressure.⁴²

In Ref. 32, two main points are important. First, it was found that the effect of propellant compressibility appears to be negligible. This is the only discussion of compressibility, and since it appears to be unimportant it will not be discussed further here. The more interesting result is that a true quasi-static calculation of the gas phase was given; in all other respects the calculation was the same as in Ref. 1. Numerical results showed that the quasi-static analysis agreed with the more involved treatment of Ref. 1 to within

10% for frequencies up to 10,000 cps, somewhat higher than one could reasonably have expected. This, of course, is the only available check of the quasi-static approximation, but it is valid only for that particular treatment of the gas phase.

The formula found in Ref. 32 [Eq. (23)] for q'_{s+} in the quasi-static limit is

$$q'_{s+}/\bar{q}_{s+} = a_0(m'_s/\bar{m}) + b_0(p'/\bar{p}) \quad (41)$$

where a_0 and b_0 are functions of propellant properties. Equation (41) is the quantity required from solution to the gas phase, and combination of the pyrolysis law, the solution for the solid phase, and the energy matching condition (25) gives

$$(m'_s/\bar{m})/(p'/\bar{p}) = n/[1 + j(J/cT_i)] \quad (42)$$

where j is the index in the burning law $m \sim p^n T_i^j$. It is particularly interesting to examine the case where the direct dependence of mass flux on heat transfer is absent ($\alpha = 0$), for which the function J is given by (40). Then Eq. (42) is easily put in the form

$$\frac{1}{n} \frac{m'_s/\bar{m}}{p'/\bar{p}} = \frac{AB}{\lambda + (A/\lambda) - (1 + A) + AB} \quad (43)$$

with $B = \tau_i/j(1 - \tau_i)$ dependent only on the solid phase. This is the form already found, Eq. (36), and it will appear shortly as the result of several other calculations as well.

It is quite easy to show from Eq. (43) that large peaks in this function will occur only for quite unrealistic values of surface activation energy¹⁸ if B is given by the formula just shown. One must conclude then, as the original authors found in their numerical work, that with the treatment of the gas phase used in these papers it may be difficult to find large values of the admittance function for realistic values of frequency and surface activation energy. The trouble seems to lie not so much with the treatment of the flame as a thin region as with the handling of the boundary conditions on the gas phase region and subsequent manipulations. It is clear from (43) that these have been set in such a way that the final result contains no parameter characterizing the gas phase.

The preceding discussion applies to the case $\alpha = 0$; for $\alpha \neq 0$ the formula for $\bar{\mu}/\bar{\epsilon}$ is much more complicated. Judging from the results given in Refs. 1 and 32, it appears that the difficulty is not avoided either by taking $\alpha \neq 0$ or by relaxing the assumption that the gas phase behaves in a quasi-static manner. The calculations of Ref. 41 are also based on the model and analysis used in Refs. 1 and 32 but with some account taken of thermal radiation by the burnt combustion gases. Radiation was included as a perturbation about a quasi-static analysis of the gas phase. This complication was added in an attempt to obtain larger values of $\bar{\mu}/\bar{\epsilon}$ with reasonable values of E and other parameters. It was found that the response was indeed slightly enhanced at the lower frequencies; a discussion of the results was also given in Ref. 46.

The last paper of this series constitutes another attempt to predict larger responses in the lower-frequency range. The principal change is that the pyrolysis law contains no dependence on heat transfer from the gas phase ($\alpha = 0$) but it does have a dependence on pressure:

$$m = B_0 [p/(T_s)]^{1/2} e^{-E_s/R_0 T_s} \quad (44)$$

This formula is based partly on the idea that "active constituents" in the gas near the solid surface may return to the surface and thereby alter the reaction rate. From kinetic theory, the flux of particles in one direction through a plane is proportional to $p/(T)^{1/2}$ which accounts for the factor in (44). Not all such collisions lead to reaction, and the weighting factor $\exp(-E_s/R_0 T_s)$ enters. Thus, the added sensitivity to pressure is associated with an "autocatalytic effect."

Once again the gas phase is treated quasi-statically, but other assumptions and details differ in certain respects from those used in Refs. 1, 32, and 41. The response function [see

Eq. (20) of Ref. 42, but note that J_a corresponds to $-J$ here] is included here in Table 1 [cf. also Eq. (51) here]; it differs from (43) only in the factor $n_s(\lambda - 1)$ in the numerator (in Ref. 42, $n_s = 1$). Although numerical calculations do show higher peaks and relatively good agreement with data (for one double-base propellant) is obtained, the values of E used are still low. A good discussion of this point as well as certain relevant aspects of steady burning is included in Ref. 42.

It is fairly clear, even from such a brief coverage, that the last paper, like the other three, contains little information about the gas phase; this part of the problem seems to be too simplified. Thus, the results shown in Table 1 for the quasi-static treatment (which were found to be in good agreement with the nonquasi-static form of the analysis¹ for frequencies up to 10,000 cps) contain no parameter characterizing the gas phase. It will be evident shortly that this is contrary to results found elsewhere for which interpretation of B is different.

The only elaborate attempt to treat diffusion is that by Williams.²⁸ However, not only is the quasi-static approximation made, but the final result for the response function m'_s/m goes to zero for $\omega \rightarrow 0$; that is, it is valid only for $n = 0$, a restrictive case at best. This unfortunate result originates mostly in approximations used to treat the steady-state behavior of the gas phase, but possibly also in the handling of the quasi-static approximation; it is not clear just where. In view of this serious failing, although the results might be valid if $n = 0$ (i.e., mesa propellants) and because the analysis is lengthy and differs from others only in the treatment of the gas phase, it will not be discussed here.

That the response function in simplest form contains, besides the dimensionless frequency, only two parameters (here denoted by A and B) was first shown by Denison and Baum.³⁰ They use the quasi-static assumption for the gas phase, and, although diffusion is ostensibly included, its influence does not appear in the final results because the Lewis number is taken to be unity. However, they unjustifiably use a result found in adiabatic laminar flame theory for premixed gases. It had earlier been shown, by von Kármán for example, that the eigenvalue problem for a simple laminar flame, effectively a flame front according to the approximations used, leads to

$$m = K p^{\nu_1} T_f^{\nu_2} e^{-E_f/2R_0 T_f} \quad (45)$$

where K , ν_1 , and ν_2 are constant, depending on the initial composition and state of the reactant gases, and E_f is the activation energy for the gas phase reaction. A calculation⁴⁴ for the more realistic case of a flame front burning in the gas phase adjacent to a solid surface gives

$$m = K p^{\nu_1} T_f^{\nu_2} [1 - (c_p/Q_g)(T_f - T_s)]^{1/2} e^{-E_f/2R_0 T_f} \quad (46)$$

in which Q_g is the heat released per unit mass in the gas phase reaction ($Q_g = \epsilon_r Q_r$ in Ref. 30). Equation (46) shows a dependence on surface temperature as one might expect, but it must still be regarded as a rough approximation so far as the chemical aspects are concerned.

The procedure for using a result of this sort, which is really the approximate solution to the gas phase problem, is common to several works. Energy conservation applied to the region between the solid surface and a position just downstream of the flame gives quite generally

$$q_{s+} = (m/\bar{m})[(T_s/\bar{T}_s) - (T_f/\bar{T}_s) + (Q_g/c_p \bar{T}_s)] \quad (47)$$

If fluctuations in Q_g are ignored, the linearized form of (47) gives

$$q'_{s+} = (m'/\bar{m})[1 - \bar{\tau}_f + (Q_g/c_p \bar{T}_s)] + \tau'_s - \tau'_f \quad (48)$$

Linearization of (45), (46), or a similar result gives a relationship between m' , p' , τ'_s , and τ'_f , which may be shown symbolically as

$$m'/\bar{m} = \nu_1(p'/\bar{p}) + Y_1\tau'_s + Y_f\tau'_f \quad (49)$$

For example, $T_\tau = 0$, $Y_f = \varepsilon$, and $\nu_1 = n/2$ in the notation of Ref. 30.

Since $m \approx m_s$ within the quasi-static approximation (49) may be used as an equation giving the fluctuations of flame temperature; substitution into (48) with m'_s determined by the pyrolysis law leads to

$$q'_{s+} = (c/c_p)X_{\tau+}\tau'_s + (c/c_p)X_{p+}(p'/\bar{p}) \quad (50)$$

which is the heat transfer provided by the gas phase. This must be equated to (27), the fluctuation of heat transfer required by processes in the gas phase. Eventually one can find $\tau'_s/(p'/\bar{p})$ and hence the response function. The result for $\tau_1 = \tau_2 = X_{p-} = 0$ is once again the familiar form

$$\frac{1}{n} \frac{m'_s/\bar{m}}{p'/\bar{p}} = \frac{AB + (n_s/n)(\lambda - 1)}{\lambda + (A/\lambda) - (1 + A) + AB} \quad (51)$$

in which, since $n_s \neq 0$, pressure dependence of the pyrolysis law is accounted for, and now the parameter B is

$$B = [X_{p+} - X_{p-} - n_s(1 - \tau_i)]/[(n - n_s)(1 - \tau_i)] \quad (52)$$

In Ref. 30, $n_s = 0$ and B is denoted by α ; AB corresponds to P of Ref. 18. Note that in (51) the correct behavior for $\omega \rightarrow 0$ has been assured by requiring $X_{\tau-} - X_{\tau+} = AB - (1 + A)$, which places a restriction on certain of the quantities introduced in the model for the gas phase. The equivalence of the real part of (51) with $n_s = 0$ and E times Eq. (71) of Ref. 30 is easily shown.

Differences between the models for the gas phase will be exhibited in whatever relationship corresponds to (45) or (46). Upon linearization, one must always obtain m'_s/m linear in p' , τ'_s , and τ'_f . All coefficients are independent of frequency for the quasi-static approximation, and it is evident that the response function must eventually have the form (51).

It is particularly important, however, that the parameter B now depends very much on properties of the gas phase and not merely on the solid phase (cf. results obtained by McClure et al.⁵⁷). The difficulty in finding large values (peaks) in m'_s/m or $\tilde{\mu}/\tilde{\epsilon}$ for reasonable values of activation energy does not arise, as shown later in connection with experiments. The shape of the real part of the response function given by (43) is quite reasonable (Fig. 2), although in certain respects agreement with experimental results is unacceptable, even qualitatively.

Friedly and Petersen³¹ have carried out a calculation that differs from that of Denison and Baum only by the use of a different, but still adiabatic, flame theory (Zel'dovitch's formulation). Consequently, the response function has the form (51) with $n_s = 0$. It appears, judging by Figs. 3 and 7 of Ref. 31, that they did not force the limiting behavior for $\omega \rightarrow 0$. They have, therefore, too many parameters free to be specified when in fact only n , A , and B can be arbitrarily set.

However, it would be surprising if a result containing only two parameters should work. For example, no account has been taken of inhomogeneities, decomposition of the solid phase in a finite region, or of the obvious differences between composite and double-base propellants. Some results relevant to the last question have been reported by Marxman.⁴⁷ The computation is basically that of Denison and Baum, but with an attempt to include "surface-coupled" reactions, and thereby improves upon the simple one-step reaction implied by the use of simple laminar flame theory. However, the calculation incorrectly makes use of the result (45) for an adiabatic flame and introduces further dubious points as well. In addition to the flame region relatively far from the surface, it is assumed that in the gas phase near the surface (effectively in the region denoted $s+$ here) two distinct contributions to the rate of energy release can be identified: an amount Q_H dependent upon the local gas phase conditions and

an amount \dot{Q}_D independent of the gas phase, the latter presumably associated with solid phase reactions. These additional sources of heat release can be incorporated either in the energy matching condition, Eq. (24), as Marxman chooses to do or as contributions to q_{s+} found in the solution to the gas-phase problem.

In either case the calculations outlined previously, with constant energy release in the gas phase Q_g but additional contributions \dot{Q}_H , \dot{Q}_D to the rates of "surface-coupled" energy release, lead to the response function¹⁸

$$\frac{m'_s/m}{p'/\bar{p}} = \frac{\nu_1 AB + E\nu_3\theta_H}{\lambda + (A/\lambda) - (1 + A) + A(B - \theta_s/A)} \quad (53)$$

where $\theta_H = \dot{Q}_D/\bar{m}c\bar{T}_s$, $\theta_D = \dot{Q}_D/mc\bar{T}_s$, $\theta_s = \theta_H(E_H/R_0\bar{T}_s - \nu_3) + \theta_D(E_D/R_0\bar{T}_s)$, and \dot{Q}_H , \dot{Q}_D have been assumed to have the forms

$$Q_H \sim m_s(p/T_s)^{\nu_2} e^{-E_H/R_0T_s} \quad \dot{Q}_D \sim m_s e^{-E_D/R_0T_s} \quad (54)$$

Here, both A and B are the same as in Ref. 30; in particular, $B = c_p\nu_1/nc\varepsilon = c_p\nu_1/nc(n + \frac{1}{2} + E_f/2R_0T_f)$. The correct limit for $\omega \rightarrow 0$ imposes the restriction

$$n = (\nu_1 + E\nu_3\theta_H/A)/(B - \theta_s/A) \quad (55)$$

which is a formula for the steady-state burning index in terms of both kinetic and thermodynamic quantities. No evidence has been reported to verify (55); accurate numerical values for most of the quantities involved are not available, so any justification must rest on estimates.

If (55) does hold, then (53) is exactly the earlier result (43), but with a new definition of B : $B' = B - \theta_s/A$. Use⁴⁷ of (53) then rests on the supposition that B is known and fixed, and the response is examined as a function of θ_s , essentially reflecting the amount of energy released in surface-coupled reactions. It is supposed that $\theta_s \neq 0$ corresponds to composite propellants and $\theta_s = 0$ to double-base propellants. The stability of motions in a chamber is qualitatively discussed in a manner treated in the next section.

However, there are some serious flaws in this calculation. It has already been noted that the same form results whether the contributions $\dot{Q}_H + \dot{Q}_D$ are associated strictly with surface energy balance or are supposed part of the heat transfer (q_{s+}) from the gas phase. This means that a response function like (53) might also be found if one permits variable energy release in the gas phase. Hence it is not possible to attribute conclusions based on $\theta_s \neq 0$ solely to surface-coupled reactions. Furthermore, it follows from the over-all conservation of energy that for a given solid and hence final flame temperature one can imagine θ_s (i.e., \dot{Q}_H and \dot{Q}_D) to be varied only at the expense of the energy released elsewhere in the gas phase flame. Therefore, the assumption that Q_g is fixed in (48) is invalid, and one must include a term Q'_g/c_pT_s .

Suppose that the total heat release ($mQ_g + \dot{Q}_H + \dot{Q}_D$) is at all times fixed (as suggested in the last source of Ref. 47). Then one finds that the term Q'_g/c_pT_s in q'_{s+} exactly cancels a term $(\dot{Q}'_H + \dot{Q}'_D)/\bar{m}c\bar{T}_s$ which represents the fluctuation of surface-coupled energy release in the interfacial energy balance. Thus, contrary to the unproved supposition of Ref. 47, variations in Q'_g are not of second order in their effect; the net result is that the final response function does not contain the parameters θ_s , θ_H , etc. In order to obtain a result like (55), it appears that a more careful account of the various contributions to the energy balance must be given, and in addition variations in the flame temperature due to variations in the total energy release must be allowed. †

† According to Marxman (private communication), such a correction is being made with results (as yet unpublished) which are consistent with experimental observations.

Reference 48 is also based on the same kind of basic calculation, and ostensibly incorporates surface reactions not identifiable as simple pyrolysis. However, it contains the incorrect assumption that the heat transfer from the gas to the solid is in phase with the pressure fluctuations. The response function found is exactly (43), although some regrouping of symbols is necessary to show this. Some relevant experimental data (from a T-burner) are included. The observations are not understood at this time, but there seems to be evidence of the effect of surface reactions other than simple pyrolysis.

All of the work discussed so far involves the assumption that purely solid phase reactions occur in a plane of infinitesimal thickness—perhaps not a good approximation, because not only is the surface rough, but there are reactions in the solid phase (decomposition) which do take place at temperatures lower than the surface temperature. The analysis of a decomposition region greatly complicates the calculations for the solid phase; the only treatment at present is in Ref. 29.† Decomposition and the associated heat release or absorption affect mainly the temperature gradients, and the response function is subsequently rather strongly affected.

The gas phase is treated with the quasi-static approximation, but the further assumption is made that the temperature fluctuation just downstream of the flame zone varies isentropically. It is then shown that independently of the details of the flame structure one finds a formula like (50) and hence the form (51) for the response function. In effect, one avoids detailed considerations of the flame structure by making the isentropic assumption. However, as later discussion elaborates, the issue merits more careful consideration, and the assumption is incorrect. The assumption of isentropic behavior can be dropped, but a relation like (45) or (46) is required to determine the perturbations of flame temperature. In any event, one ultimately finds the same form for the response function.

As additional refinements are included, the number of parameters increases; so far, apart from Ω , only B , n_s , and A appear in (51). These three depend on particular properties of the propellants (such as T_s , E_s , T_i , etc.), but the point is to group these into the simplest combinations. In Ref. 29, there are four associated with the decomposition region, two (besides A) for the burning surface, with only B for the gas phase. The interpretation but not the precise value of these is known.

A recent calculation⁴⁹ dealing with the problem of the flame structure leads once again to the form (43). The gas phase is modelled as a region of uniform energy release extending from the solid to some position, the flame thickness. Both incorrect use of a result for adiabatic flame theory and the assumption of isentropic temperature fluctuations at the edge of the flame are avoided. However, the calculation does involve some detailed estimates and approximations which need not be used. The analysis based on this model can be carried out "exactly"⁴⁴ and leads to a formula similar to (46).

Self-Excited or Intrinsic Instabilities

It has already been noted that Green, Dension and Baum, and others have attempted to identify the occurrence of infinite values of $(m'/m_s)/(p'/p)$ with the conditions for oscillations in a rocket motor. If the response is indefinitely large, then an infinitesimally small pressure change (unavoidably present in a real chamber) causes a large fluctuation in the mass flux, which in turn reinforces the original pressure disturbance. In some earlier works this process, presumably leading also to increases in the mean burning rate, was called "resonance," as opposed to "sonance," the occurrence of relatively small amplitude oscillations. This usage of the

† In a paper which was not known to the author until recently, S. S. Novikov and Yu. S. Ryaxantsev (PMFT, 1965, in Russian) have reported work similar in certain respects to that Ref. 29.

terms has fortunately disappeared. Such an event has nothing to do with oscillations in the chamber, and in fact would occur at frequencies determined by the propellant (see below). An inherent, or intrinsic, or self-excited instability of this sort may be possible (it has not been proven experimentally) but is almost certainly not the kind of instability present in rocket chambers. It seems quite clear that the over-all problem involves both strong coupling (expressed as a response function) of the burning solid to the gas phase, and the geometry of the chamber. This combination mainly determines the frequency of motions, whether they be standing or traveling waves.

However, it is true that the propellant most strongly drives oscillations in the frequency range where the real part of the response function is largest, and this occurs rather close (in a sense shown below) to the infinite values.²⁹ As an aid to qualitative argument, it is indeed useful to locate the poles of the response function. It happens that this is very simply done for the form (51). The denominator vanishes if

$$\lambda(\lambda - 1) + \lambda A(B - 1) - A = 0$$

This gives a formula for λ which, when substituted into (17), gives for the real and imaginary parts of Ω

$$\Omega_r = \pm \frac{1}{2}A(B - 1)[4A - (A - AB + 1)^2]^{1/2} \quad (56)$$

$$\Omega_i = A + \frac{1}{2}A(B - 1)(A - AB + 1) \quad (57)$$

Now Ω originally appeared as the frequency of harmonic time variations, so that if $i\Omega$ is regarded as a Laplace transform variable, $\Omega_i \geq 0$ for stable transient motions. This condition, with (57) rearranged, gives

$$(B + 1) \geq A(B - 1) \quad (58)$$

Equality holds on the boundary between stable and unstable motions; (56) then gives

$$\Omega_r = A(B)^{1/2} \quad (59)$$

This is a useful formula for estimating the location of the maximum in the response function. Note that the frequency at which the peak occurs increases with both surface activation energy and B , which is a measure of the sensitivity of the gas phase and surface pyrolysis to pressure perturbations [cf. Eq. (52)].

Equation (58) is plotted as the limiting line in Fig. 1 of Ref. 30. Marxman⁴⁷ has used the shift of this limit for changes of B' due to θ_s in Eq. (53); the shift is in different directions for different signs of θ_s . Although experimental evidence is reported to support the theoretical predictions, in view of the discussion in the preceding section the interpretation must remain unconvincing until further work is done. A similar shift can be found from the analysis of Ref. 29, except that A rather than B effectively is altered. One can show that in the limit of small Q and l one has again (43), except that A is replaced by $A - Ql^2/2$; l is the dimensionless thickness of the decomposition region and Q is the normalized heat release. Use of (58) should be regarded as a qualitative indication of trends and not as support of the view that the oscillations are self-excited.

Isentropic or Nonisentropic?

Several years ago, an interesting question was raised by Summerfield^{50,51} regarding the behavior of the coupled burning and pressure oscillations, particularly at low frequencies. Although the oscillations in the burnt gases may apparently, to a good approximation, be regarded as isentropic, if they are small amplitude waves, the assumption is less credible in the region near the flame. The boundary condition required for analysis of the chamber problem is the normal velocity component produced by a small pressure change. However, this depends also on the density (or temperature) changes associated with the pressure fluctuation, as shown by Eqs. (1)

and (2). The second term in the bracket of (2) is unity only if the process is isentropic at the edge of the burning region, which must be considered thin so far as the entire chamber is concerned. Moreover, the "edge" must constitute a proper outer boundary to solution of the unsteady combustion problem; for example, it is convenient to retain the assumption that the pressure is uniform but varying in time within the region analyzed for the response function.

The point raised by Summerfield concerns the validity of the common assumption that at the edge of the boundary the fluctuations are isentropic so that $\gamma(\rho'/\rho)/(p'/p) = 1$. Certainly this is not the case within the flame, so that successive elements of the flow passing through have different values of entropy. The possibility exists that these entropy variations persist to the downstream edge of the flame region and are carried with the flow. If $s e^{i\omega t}$ is the fluctuation in entropy at the downstream edge $x = \delta$ of the flame, then it is easy¹⁸ to show that the real part of the entropy perturbation is

$$s' = s'_0 \cos\{\omega t - [\omega(x - \delta)/\bar{u}]\}$$

and as a function of x there is an entropy wave of wavelength $2\pi\bar{u}/\omega$ which is much smaller than the acoustic wavelength $2\pi\bar{a}/\omega$.

Of course, there are dissipative actions tending to smooth out entropy variations so that the fluctuations s' decay as they propagate away from the flame. If s' is negligible at some plane $x = x_f$ and the region $0 < x < x_f$ is "thin," then the admittance function may be computed with the isentropic condition and the result used as a boundary condition on the waves in the chamber. The damping length is quite large⁴⁵ if only ordinary thermal conduction is accounted for; the influence of viscous stress is even less important.

Thus, apart from the certain influence of turbulence, it appears that entropy waves, if they are present, are not significantly attenuated near the surface. Arguments have been advanced⁴⁹⁻⁵² that the existence of such waves is more likely in the low-frequency range, although observation of them has only recently⁵³ been tentatively successful. One does not, of course, observe the entropy waves directly, but the associated periodic temperature variations can be measured.

The two limiting cases are isothermal and isentropic temperature variations; in the first instance $s'_0 = -R_0(p'/\bar{p}t)$ at the edge of the flame ($\tau'_f = 0$), and in the second $s'_0 = 0$. A fairly elaborate calculation exhibiting intermediate values, using Ref. 1 as a basis, has been given in Ref. 45. Very little change in the response function was found except at low frequencies and at higher frequencies where the analysis is not valid.

A much simpler calculation, restricted to very low frequencies, appears in Ref. 52. A formula for q'_{s+} was found simply by linearizing the steady-state form of the energy matching condition. Since the gas phase effectively is not considered, no parameter associated with it appears in the response function that is shown in Table 1. The more recent analysis⁴⁹ cited previously leads very nearly to the same result (Table 1), although as noted earlier more careful consideration is given to the gas phase. As one would anticipate, the response function in both cases has the two-parameter form (43).

Now a major point of those calculations was to show, as they did, the presence of nonisentropic temperature fluctuations τ'_f at the downstream edge of the flame. Indeed, this is a necessary consequence of the scheme outlined earlier [Eq. (45)ff.] One has the choice of using an independent result like (45) or (46) for the gas phase; then the necessary values of τ'_f are found; or such a result is ignored (as in Ref. 29) and τ'_f is specified. The latter course is convenient, but incorrect, even though the ultimate form of the response function is insensitive to the alternatives.

Correctly done, the procedure is simple. After both m'/\bar{m} and τ'_s have been found, τ'_f can be determined from either (45) or (49). The temperature fluctuations τ'_f are frequency

dependent. Some numerical results are given in Ref. 49; τ'_f vanishes for $\omega = 0$ but is never precisely isentropic. If, on the other hand, one assumes $\tau'_f = kp'/\bar{p}$ (k a real constant), which contains the isentropic case, then according to (49) with $Y_\tau = 0$ one has $m'/\bar{m} = (\nu_1 + kY_f)(p'/\bar{p})$. However, $\nu_1 + kY_f$ is real, and this relation is supposed to hold always, in particular for all frequencies; this contradicts the result one finds later for the dependence of the response function on frequency. Hence, a priori specification of the relation between pressure and temperature fluctuations at the downstream edge of the flame cannot in general be reconciled with the global behavior of the gas phase, as expressed in a formula like (46). One must determine the temperature fluctuations as part of the calculation.

The answer to the question posed, then, is that the motions are not isentropic at the edge of the flame. Correspondingly, there must be short wavelength entropy or (unless the flame edge is isothermal) temperature waves emitted from the flame zone. Sufficiently sensitive experimental observations should find them. Their properties may provide information about the behavior and character of the combustion region in the gas phase. Moreover, it should be emphasized that for a correct treatment of the instability of waves in a chamber, one needs the admittance function, Eq. (2), not merely m'/p' . Thus, values of the temperature fluctuations are required in order to determine the second term in Eq. (2).

Comparison with Experimental Results and Concluding Remarks

From the practical point of view, the importance of the response function arises from its central position in the problem of combustion instability (see Ref. 58, for example). The more immediate purpose of the calculations discussed here is to motivate interpretation of experimental results and thereby classify propellants according to a small number of parameters. Such information would clearly be directly useful in design and development work. Quite obviously, the problem is too complicated to be analyzed quantitatively in all respects. On the other hand, the simplest existing computations which have been reviewed here fall short of accommodating a substantial number of measurements.

It has been shown here that almost all of the recent comprehensive analyses lead to the two-parameter form for the response function, Eq. (43) (see also Table 1), or three parameters if the surface pyrolysis is assumed to be pressure dependent, $n_s \neq 0$. Since the response function is complex, both the real and imaginary parts must be taken into account when comparison is made with experiments. The first discussion in which this has been done appears in Ref. 54; measurements for three propellants (two composite and one double-base, JPN) are treated, with $n_s = 0$. Data can be interpreted only by combining the response function with an analysis of the laboratory device used, either a T-burner or an L* burner at the present time. In both cases, it is possible to construct a chart on which raw data (frequency and growth constant of the oscillations can be entered and the associated values of A and B may be read directly.

Data from an L* burner, when treated in this way, give reasonable results only for one of the composite propellants (A-35). The value of $A = 14$ suggests a surface activation energy in the range commonly quoted from other pyrolysis measurements, and $B = 0.8$ is of the order one finds from both Refs. 30 and 42, for example. A plot of the real part of the response function is shown in Fig. 3, with both L* and T-burner data; note that the influence of including surface reactions dependent on pressure can be significant in the higher frequency range. Measurements in an L* burner for the other composite propellant (A-13) imply a negative value of A if the approach based on an L* chart is used. On the other hand, if one ignores the phase or imaginary part, the trends of the data can be roughly matched with $A = 40$,

$B = 1.1$ as shown in Fig. 4. It does not seem to be possible, however, to obtain good agreement in both the high-frequency (T-burner) and low-frequency (L* burner) ranges.

Important qualitative differences are also shown by the double-base propellant JPN when T-burner data⁷ are interpreted by means of the chart mentioned previously. However, as for the composite propellant A-35, it is possible to match the data fairly well by appropriate choice of A and B , if one tries to fit only the real part of the response. Such a treatment appears in Ref. 42 for the data of Ref. 7.

Similar discrepancies have been found by application of the same method of interpretation to several other composite propellants,⁵⁵ based on measurements in an L* burner. Those results also show some effects of changing oxidizer particle size, a feature that is not included in the calculations discussed here. Moreover, there is a trend with pressure level, shown in Fig. 4 and less in Fig. 3, which also seems to lie outside the validity of the calculations (see also the data of Ref. 7). It is true that A must vary with pressure level because the surface temperature does; as the pressure and hence burning rate increase, then so does the surface temperature if the simple pyrolysis law (25) is valid. Hence, A decreases with pressure; also, B changes, but neither of these seems⁵⁴ to accommodate the observations. For some propellants, the index n is not constant with pressure level. For $n \neq 0$, this is easily handled within the calculations presented here, a significant effect; the case $n = 0$ has not been satisfactorily treated.

The differences between the theoretical predictions and the measurements seem to be much too large to be attributed to approximations involved in the analyses of the burners. Hence, the results cited constitute ample evidence that the form (43), even with $n_s \neq 0$, is not generally valid. Significantly, however, the shape of the response function predicted by this formula is quite representative. As a function of frequency, as in Figs. 3 and 4 here, all measurements of the real part show a pronounced peak in the region of a few hundred to several thousand cycles per second, decaying to small values at higher frequencies. This qualitative behavior is wholly a consequence of the thermal wave in the solid phase, since the gas phase is assumed to behave quasi-statically. If attention is confined to the real part, then the analytical result appears to be acceptable; it is when the real and imaginary parts together are compared that the limitations become apparent.

Because these analyses contain in common the four basic assumptions listed in the Introduction, it is reasonable to examine those more closely. Some of the disagreement might be resolved by incorporating condensed phase reactions, as in Ref. 29. A comparison of those calculations with data has not been carried out; although this probably ought to be done, it would be somewhat tedious because of the number of unknown parameters. The shape of the real part of the response functions is not qualitatively changed, but the increased freedom in fitting the data may produce reasonable results.

It is the author's belief at the present time that the first and last assumptions listed may well be equally suspect. Before one can confidently apply the calculations to composite propellants, it is certainly necessary at least to show how good the approximation of a homogeneous solid really is. Some data in Ref. 55 suggest very strongly that certain three-dimensional features are unavoidable.

The quasi-static approximation may conceal even more. It is clear from the analyses reviewed here that it is difficult to distinguish between models of the gas phase when this assumption is used. All models lead to the two-parameter form (43) and uncertainties in numerical values of the physical quantities involved tend to obscure genuine differences. This fact unfortunately detracts from the simplicity of the results. Moreover, the assumption itself may (as some of the comparisons with data indicate) fail at lower frequencies than

the crude estimates lead one to believe. The essence of the approximation is that, at any instant of time, for the existing values of temperature and other property values (composition, etc.) at the boundaries of the gas phase, the profiles and hence in particular the heat transfer at the surface are given by the formulas deduced in an analysis of the steady state. These can then be perturbed to give T'_f , q'_{s+} and so forth. This procedure does not mean that the heat transfer is the same as that for a steady state at the same pressure nor that the fluctuations (T'_f , etc.) are independent of frequency, but it does imply that all processes in the gas phase respond so rapidly that all variations with frequency are ultimately due to the thermal wave in the solid. It is likely that differences between models of the gas phase will become more obvious if this restriction to "low" frequencies can be relaxed.

Nonlinear calculations should also be much more sensitive to the model chosen for the gas phase. At the present time there exists only a small amount of work^{47,49} on this aspect of the problem. The results so far are incomplete and there appears to have been no attempt to compare with measurements.

It is clear that much remains to be done before measurements will be acceptably correlated and before the various parameters are related even in a gross way to the composition of the propellant. At the same time, there are several important pieces of the problem which have not been satisfactorily analyzed: the differences between double-base and composite propellants; the response of a propellant with metallic particles; the response of plateau ($n = 0$) propellants; the question of a nonplanar, rough, solid surface, which is necessarily the case for composite propellants; velocity coupling; other nonlinear problems; and extension of results to frequencies outside the "quasi-static" range of the gas phase. Moreover, the connection between the dynamical behavior studied here and the more severe transients associated with both ignition and extinguishment has not been clarified.

On balance, however, it is quite remarkable that the simple formula (43) [or (51)] represents the measured behavior as well as it does. That this can be isolated as the consequence of the principal assumptions listed in the introduction simplifies considerably the development of more complicated analyses. If it is clear, for example, that merely constructing more realistic models of the flame structure in the gas phase without altering one or more of the basic assumptions will lead to the same formula. In this sense, only one model of the process, defined of course by the approximations used, has been treated by most of the calculations reported up to the present time.

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