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A UNIFIED THEORY OF SOLID PROPELLANT IGNITION. PART 1. DEVELOPMENT OF MATHEMATICAL MODEL

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Naval Weapons Center
China Lake, California

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(U) *A Unified Theory of Solid Propellant Ignition. Part 1. Development of Mathematical Model*, by H. H. Bradley, Jr. Chinal Lake, Calif. Naval Weapons Center, August 1974, 36 pp. (NWC TP 5618, Part 1, publication UNCLASSIFIED.)

(U) The governing equations of solid propellant ignition is one space dimension are derived from conservation and transport considerations. The resulting mathematical model contains as subcases the existing gas phase, solid phase, and surface ignition theories. More important, it allows the effect of the site of chemical reaction on the ignition transient to be examined with consistent and compatible boundary conditions. Surface regression and the first order effect of nonunity Lewis number are retained to allow examination of the effect of these phenomena which are often neglected. Several second order terms are dropped from the more general equations in the interest of mathematical tractability; these include variable specific heat and transport coefficients. Finally, the physical equations are transformed for computer coding. The computer program and results of a parameter study will be published as separate reports.

Naval Weapons Center
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FOREWORD

This report was prepared as part of a research program at the Naval Weapons Center on the subject of Solid Propellant Rocket Ignition, sponsored under Naval Ordnance Systems Command Task Assignment ORD 331-001/200-1/UR 024-02-02. A previous report (NAVWEPS Report 8937, NOTS TP 3954), summarizes the then-current status of the solid phase, heterogeneous, and gas phase theories of solid propellant ignition, and shows that comparison of their results or experimental evaluation of their relative merits was not possible because of incompatibilities of assumptions used in the analyses. Following this, extended analyses were published on solid phase ignition theory (NWC TP 4618) and heterogeneous ignition theory (NWC TP 4864). The present report is Part 1 of a series of three documents on a Unified Theory of Solid Propellant Ignition. It describes a formulation of the general propellant ignition problem, encompassing gas phase, surface, and condensed phase reactions in one-dimensional representation, with boundary conditions chosen to be compatible with the "constant-flux-radiation" type of experiment. Part 2, describing a computer program for solving the relevant equations, and Part 3, discussing results of a parameter study, will be published separately.

This report has been prepared for timely presentation of information. Because of the continuing nature of research in this area, refinements may be made in the future.

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Appendixes:

NOMENCLATURE

A_i, B_i	Constants in Eq. 79. See Key, following this Nomenclature for defining expressions
$b_i, \dot{b}_i$	Stoichiometric coefficients for bulk and surface reactions Defined in Section 3.2.2
C, C_{av}	Specific heat and average specific heat per unit mass
c	Molar concentration
$D, \mathcal{D}$	Coefficients of mass diffusion
d	Total derivative operator
E_i	Activation energy. Explanation of numerical subscripts given in Section 3.2.2
F7,F8	Reaction orders of fuel in gas phase reactions
H	Total specific enthalpy per unit mass, including chemical and thermal
h	Thermal specific enthalpy per unit mass
h^r	Reference enthalpy
I_∞	Unattenuated initiating flux density
j	Diffusion mass flux density
k_i	Mass source. Explanation of numerical subscripts given in Section 3.2.2
Le	Lewis number $= \rho C \mathcal{D}/\lambda$
m_i	Surface mass flux density. Explanation of numerical subscripts given in Section 3.2.2
O7,O8	Reaction orders of oxidizer in gas phase reactions
p	Pressure

Q_i	Heats of reaction, positive Q being exothermic. Subscripts 1, 7 and 8 correspond to reactions 1, 7, and 8 (see Sections 3.2.2.1 and 3.2.2.2). Subscripts 5, 6, 10, 11, and 12 correspond to the equivalent subscripts on n_i
q	Total thermal flux density relative to mass average phase velocity
q_r	Radiant heat flux density
q_s	Surface rate of heat evolution
R	Universal gas constant
r_i	Chemical reaction rate (see Sections 3.2.2.1 and 3.2.2.2)
S_i	Surface sources. See Key for defining expressions
$S5, S6$	Reaction orders of oxidizer in surface reactions
T	Temperature
t	Time
U	Total specific internal energy per unit mass
u	Velocity relative to stationary coordinate system
V_i	Volumetric sources. See Key for defining expressions
v	Mass average velocity
v_i	Diffusional velocity of species i
X_i	Mole fraction of species i
x	Space coordinate
Y_i	Mass fraction of species i (see Eq. 42 and 46-54 for subscript meanings)
Y_{fc}	Initial solid fuel mass fraction
Y_{og}	Initial gaseous oxidizer mass fraction
Z_i	Generalized dependent variable; includes mass fraction and enthalpy. $Z_i = Y_i$ for $i = 1, 2, \ldots 12$, $Z_{13} = h_g$, $Z_{14} = h_c$

α	Coordinate transformation parameter (see Eq. 73 and 76)
β	Flux attenuation coefficient
λ	Coefficient of thermal conductivity
μ_i	Molecular weight of species i
ν_i	Pre-exponential factor in rate expressions. Subscript i corresponds to subscript i on E
ρ	Mass density
ϕ	Transformed coordinate
ψ	Howarth transformed space coordinate
∇	Gradient operator
∂	Partial derivative operator

Subscripts

c	Condensed (solid phase)
g	Gas phase
s	Surface (interface)
o	Initial
i	Referring to species i unless otherwise specified

Key to numerical subscripts

$A_i = \alpha_g/\rho_{go} \quad : i = 1, 2, \cdots 9 \text{ and } 13$

$\quad = \alpha_c/\rho_{co} \quad : i = 10, 11, 12, 14$

$B_i = Le A_i \rho_g \lambda_g / c_g \quad : i = 1, 2, \cdots 9$

$\quad = 0 \quad : i = 10, 11, 12$

$\quad = B_1/Le \quad : i = 13$

$\quad = \alpha_c \lambda_c / c_c \quad : i = 14$

$S_i = 0 \quad : i = 1, 3, 7, 8, 9$

$S_2 = -\mu_2 b_2' m_5/\mu_{10}$

$S_4 = -\mu_4 b_4' m_6/\mu_{10}$

$S5 = \mu_5 b_5 m_5/\mu_{10}$

$S_6 = \mu_5 b_6 m_6/\mu_{10}$

$$S_{1314} = \begin{cases} q_s \text{ (see Eq. 62)} & \text{: with subsurface absorption of radiant flux} \\ q_s + q_r & \text{: no subsurface absorption of radiant flux} \end{cases}$$

$V_i = 0 : i = 3, 5, 6, 9$

$V_1 = -\mu_1(r_7 + r_8)/\rho_g$

$V_2 = -\mu_2 b_2 r_7/\rho_g$

$V_4 = -\mu_4 b_4 r_8/\rho_g$

$V_7 = \mu_7 b_7 r_7/\rho_g$

$V_{10} = -\mu_{10} r_{10}/\rho_c$

$V_{11} = -\mu_{11} b_{11} r_{10}/\rho_c$

$V_{12} = \mu_{12} b_{12} r_{10}/\rho_c$

$V_{13} = \mu_1(Q_7 r_7 + Q_8 r_8)/\rho_g$

$$V_{14} = \begin{cases} \mu_{10} Q_1 r_{10}/\rho_C & \text{: no subsurface energy absorption} \\ \mu_{10} Q_1 r_{10}/\rho_C + (\beta_C q_r/\rho_C)(1 + \phi)^{\beta_C/\alpha_C \rho_C} & \text{: with subsurface energy absorption} \end{cases}$$

1. INTRODUCTION

Combustible or explosive ingredients are an essential component of ordnance items ranging in size from small arms to long range missiles. Solid propellant charges for these devices consist of premixed fuel and oxidizer combinations which must remain in a metastable state throughout the useful storage life of the item. Ignition is the stimulation of the material by any of various energy sources, overcoming the metastable barrier. The term ignition, as used in this report, is primarily concerned with such stimulation at and near the propellant surface. Depending upon the application, there may or may not be an identifiable period of steady state operation.

In a rocket motor, between initiation and final burnout, there occurs a series of interrelated processes including mass diffusion, chemical reactions, fluid dynamics, and heat transfer by various modes. In order to simplify the ignition problem and to place the current investigation in proper perspective, it is instructive to consider three phases of ignition. First, energy from the initiator is directed toward the propellant surface. The ensuing physicochemical processes lead to self-accelerating reactions with evolution of gaseous products. Second, the locally ignited state of the propellant is propagated over the surface of the propellant by thermal and fluid dynamic means. Third, and often simultaneously, the gases evolved from the igniter and propellant produce a pressure build up in the device, leading to some desired operation. Various aspects of the latter two phases have been treated elsewhere[1-4]

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[1] de Soto, S. and H. A. Friedman. "Flame Spreading and Ignition Transients in Solid Grain Propellants," AMER INST AERON ASTRONAUT J, Vol. 3, No. 3 (March 1965), pp. 405-12.

[2] United Technology Center. *Studies on Ignition and Flame Propagation of Solid Propellants, Final Report Covering the Period 22 June 1966 through 22 June 1967,* by J. D. Kilgroe, 13 November 1967. (UTC 2229-FR prepared for Jet Propulsion Laboratory, NASA, Pasadena, Calif.)

[3] Peretz, A., and others."Starting Transient of Solid-Propellant Rocket Motors with High Internal Gas Velocities," AMER INST AERON ASTRONAUT J, Vol. 11, No. 12 (December 1973), pp. 1719-27.

[4] Bradley, H. H., Jr. "Theory of a Homogeneous Model of Rocket Motor Ignition," (January 1964, AIAA Preprint 64-127). 6 pp.

and are not considered to be within the scope of the current study. It is toward the theoretical aspects of the first phase, which is called propellant ignition, to distinguish it from rocket motor ignition, that we now direct our attention.

1.1 BACKGROUND AND REVIEW

An extensive review of solid propellant ignition theories was published in 1966.[5] It was noted there that the distinguishing features of the theories were: (1) the assumed site (solid phase, gas phase, or interface) of the key chemical process leading to an approach to steady-state combustion through a self-accelerating (due to increasing temperature) and self-limiting (due to reactant depletion and diffusional effects) reaction rate; (2) the nature of the ignition stimulus (radiant energy, hot gas or solid, or hypergolic chemical reaction); and (3) choice of an ignition criterion (e.g., critical temperature, go/no-go, light emission, or rate of temperature rise).

The earliest theory chronologically and the simplest mathematically was the solid phase thermal theory which was an outgrowth of thermal explosion theory. In it, a solid phase homogeneous reaction is predicated (justified by known solid phase exothermic reactions in double-base propellants) with the ignition stimulus consisting of a radiant source, hot gas, or hot solid. An obvious deficiency of the solid phase theory was its ability to predict or explain fully the experimentally observed effects of ambient gas conditions (pressure and composition) upon ignition time. The gas phase theory was developed in connection with an experimental program in which a solid fuel was ignited by high temperature oxidizer gas heated in a shock tube. Several versions of the gas phase theory have been presented with different degrees of sophistication; all contain the feature that fuel vapors, produced by heat transfer from the hot oxidizer to the solid, diffuse into the gas phase and subsequently react. The interface theory grew out of experimental observations in which a highly energetic oxidizer, viz., fluorine, ignited a solid fuel hypergolically at room temperature. The chemical reactivity was assumed to be confined to the surface; hence, the theory has been referred to as hypergolic or heterogeneous. This latter terminology should not be construed as denoting relevance to heterogeneous (composite) propellants, although results of the analysis have been extended heuristically to include such an application.

In addition to differences in formulation of the three theories, there has been a diversity of choice, both in experiment and theory, regarding the attainment of ignition. Experimentally, use has been made of light emission as recorded by photodetectors, pressure or temperature rise, behavior of the propellant sample after interruption of the

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[5] Price, E. W., and others. "Theory of Ignition of Solid Propellants," AMER INST AERON ASTRONAUT J, Vol. 4, No. 7 (July 1966), pp. 1153-81.

ignition stimulus, and physical examination of the specimen after quenching. In theoretical models the attainment of a given surface temperature (often called the ignition temperature), rate of temperature rise or of chemical heating, or mathematical solution of the equations after interruption of external heating have been employed. Only limited work has been done in a effort to correlate the different ignition criteria, but it is known that the definition of ignition is important

1.2 PURPOSE OF CURRENT STUDY: UNIFIED IGNITION THEORY

While there has been reasonable agreement between experimental ignition results and a particular theory (probably by purposeful design), lack of common and compatible assumptions has hindered comparisons among theories and between theories and experiments.[5] Hence, the same experimental data have seldom if ever been subjected to several alternative theoretical interpretations. One purpose of this investigation is to facilitate comparison of theories and experiment by constructing a model including chemical processes at any or all of the usually selected sites, but otherwise containing compatible and consistent assumptions. Results of solving the model equations are not expected to substantiate any particular ignition theory to the exclusion of all others; instead, the results will probably reveal combinations of parameters for which each reaction site (solid phase, surface, gas phase) is dominant in ignition. Many of the physical quantities involved are not accurately known; hence, quantitative testing of the theory is not possible at present. Nevertheless, the unified ignition model should enable calculations of important sensitivity relationships between parameters and solutions as well as meaningful comparison with results from appropriately designed experiments.

A second important purpose of the study is the determination of the importance of some of the common assumptions which are often made to simplify the mathematical treatment of the equations. Examples are inclusion or exclusion of surface regression, gas phase convection with consequent blocking of heat conduction to the surface, and equality of the thermal and mass diffusivities (the assumption of unity Lewis number).

2. PHYSICAL DESCRIPTION OF PROBLEM

Consider the transient one-dimensional system in Figure 1. Initially, a condensed phase, containing fuel and oxidizer ingredients, occupies the region $x < 0$ while a gas phase, consisting of oxidizer and inert ingredients, fills the region $x > 0$. In general, different uniform initial temperatures are permitted for each phase. At time zero an ignition stimulus consisting of a time-dependent flux is directed at the interface from a remote position in the gas phase. Conditions remote from the interface are maintained at their initial values. The ensuing response of the system may in general include:

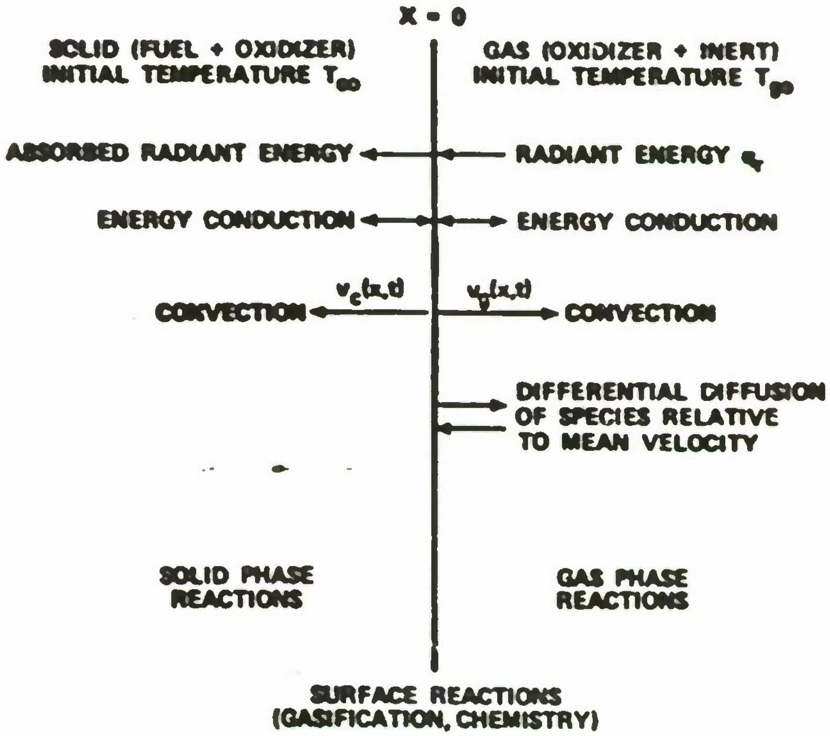

FIGURE 1. Schematic Representation of Unified Ignition Model .

1. Bulk chemical reactions confined to one or both homogeneous phases. In the solid phase, the reaction occurs either between fuel and oxidizer or may consist of a pyrolytic decomposition of the solid phase to provide a reactive fuel and oxidizer which participate further in surface or gaseous reactions. In the gas phase, reactions may take place between pyrolyzed fuel and either pyrolyzed oxidizer or oxidizer originally present as a gas phase ingredient.

2. Interface processes, consisting of chemical reactions or pyrolysis, in which two phases are involved.

3. Motion of the phase boundary owing to mass transport across the boundary. In this model, the motion is induced solely by surface processes, either pyrolytic or reactive in nature.

4. Gaseous diffusion of all species, either reactants or products.

5. Absorption of the stimulation radiant flux by the solid phase or by evolved gases.

6. Heat transfer by conduction and convection.

In the following mathematical section, the appropriate governing equations are developed whose solutions describe the relationships of dependent variables (concentration and enthalpy or temperature) to independent variables (time and position).

3. MATHEMATICAL FORMULATION

The equations which describe the behavior of the present system consist of conservation equations and constitutive equations combined to give the governing equations. The former are general and independent of the nature of materials involved; the latter represent empirically observed relationships among the variables appearing in the conservation equations and are required, with the initial and boundary conditions, to provide a complete set of equations. The conservation equations may be further classified as field or interface equations.

In the derivations which follow, a stationary coordinate system relative to the observer is established at the phase interface. Physically, the model behaves as if material in the solid phase approaches the boundary from the left (see Figure 1) at a velocity which varies with time,* crosses the phase boundary, while undergoing substantial physical and chemical changes, and flows away toward the right with a velocity which is a different function of time and position. All properties are assumed constant along planes parallel to the interface, so that the model is adequately described by transient equations of one space dimension.

3.1 CONSERVATION EQUATIONS

The relationships expressing conservation of mass, momentum and energy are derived and presented in numerous standard works (for example, see Footnote 6). In the current study, the effects of gravity, differential external force fields such as electrostatic force fields, and viscosity are neglected; and gas velocities are assumed to be low enough so that pressure

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*The solid phase bulk density may vary due to differences in density among the reactants and solid products, but, more importantly, due to subsurface evolution of gaseous products. Such phenomena are neglected in the present study; evolution of gas is presumed to occur only at the surface, and solid phase reactions are assumed to occur without density changes. For these reasons, the solid phase velocity does not vary with position.

[6] Bird, R. B., W. E. Stewart and E. N. Lightfoot. *Transport Phenomena.* New York, Wiley, 1960. 790 pp.

gradients and kinetic energy contributions need not be considered. The usual Euler or Navier-Stokes equation of motion is simplified to the condition of constant pressure (spacewise). The mathematical description of the problem then is reduced to equations representing mass and energy conservation for each bulk phase (field equations) and the interface.

3.1.1 Field Equations

3.1.1.1 Species Conservation. The mass balance of species i for a stationary element of volume is given by

$$\frac{\partial(\rho Y_i)}{\partial t} = - \frac{\partial(\rho Y_i u_i)}{\partial x} + k_i \tag{1}$$

where ρ is the density of the medium, and Y_i, k_i and u_i are mass fraction, rate of production, and velocity of species i relative to the stationary coordinate system. By summing Eq. 1 over all i and noting that $\Sigma Y_i = 1$ and $\Sigma k_i = 0$, one obtains the equation for overall mass conservation

$$\frac{\partial \rho}{\partial t} = - \frac{\partial(\rho v)}{\partial x} \tag{2}$$

Equation 2 defines

$$v \equiv \Sigma Y_i u_i \tag{3}$$

as the mass average velocity, usually identified as the hydrodynamic (Pitot tube) velocity. This barycentric description is adopted because of its formal advantage over molar or other descriptions in handling problems dealing with simultaneous convection and diffusion. We may now write Eq. 1 in an alternate form which is more convenient for calculation purposes. We first define

$$v_i \equiv u_i - v \tag{4}$$

as the species mass velocity relative to the local mass average velocity. The product

$$\rho Y_i v_i \equiv j_i \tag{5}$$

represents the mass diffusional flux of species i relative to the local mass average velocity. By substituting Eq. 4 and 5 into 1 and making use of Eq. 2, one may derive

$$\rho \frac{dY_i}{dt} \equiv \rho \frac{\partial Y_i}{\partial t} + \rho v \frac{\partial Y_i}{\partial x} = - \frac{\partial j_i}{\partial x} + k_i \tag{6}$$

as the expression for species conservation.

3.1.1.2 Energy Conservation. The fundamental derivation of energy conservation is in terms of specific internal energy of a stationary volume element and leads to

$$\frac{\partial}{\partial t} (\rho U) = - \frac{\partial}{\partial x} (\rho U v) - \frac{\partial q}{\partial x} - p \frac{\partial v}{\partial x} \tag{7}$$

where the specific internal energy U is made up of thermal and chemical components.

The reduction of the momentum equation to p = constant makes it desirable to eliminate the final term, containing $\partial v/\partial x$, from Eq. 7. This may be accomplished by making use of Eq. 2 and the definition of enthalpy (including thermal and chemical).

$$H = U + p/\rho \tag{8}$$

The final result is

$$\rho \frac{dH}{dt} \equiv \rho \frac{\partial H}{\partial t} + \rho v \frac{\partial H}{\partial x} = - \frac{\partial q}{\partial x} + \frac{\partial p}{\partial t} \tag{9}$$

The quantity q represents heat transferred relative to the mass average velocity and in general includes heat conduction owing to temperature and concentration gradients, transport of the intrinsic energy of diffusing species, and radiation. In principle, photochemical heat release could also be included if details of the process were available for the purpose of establishing the effect on the mass conservation equations. The final term, $\partial p/\partial t$ is what remains of the more general term

$$\frac{dp}{dt} = \frac{\partial p}{\partial t} + v \frac{\partial p}{\partial x} \tag{10}$$

when spacewise pressure variations are neglected. In the following sections, $\partial p/\partial t$ is also ignored; for purposes of studying dynamic pressure effects it could readily be reintroduced.

3.1.2 Interface Equations

The boundary between two phases is physically a finite region, through which the properties are continuous and governed by the same conservation laws that are valid for a homogeneous phase. The principal distinguishing features of the interfacial region are the relatively large spatial derivatives of the properties, the small dimensions compared to other physical dimensions of the system, and a large change in relative importance of various microscopic force terms as the interfacial zone is traversed. Examples are crystal lattice forces and binding forces of activated chemical complexes associated with catalytic reactions. It is convenient in the current discussion to bypass the details of such phenomena and to regard the interface as a mathematical surface of discontinuity joining two continuous phases. In this spirit, it is assumed that no accumulation of mass or energy occurs at the interface.

3.1.2.1 Species Conservation. If we ignore molecular diffusion in the solid phase, the mass balance of species i at the surface is

$$m_{cis} + k_{is} = m_{gis} + j_{gis} \tag{11}$$

The m terms represent convective mass transport owing to bulk velocity of the phase which arises from surface chemistry or pyrolysis, k is the rate of formation of species i in surface processes, while j is the gaseous mass diffusion rate. Total mass conservation is obtained by summing Eq. 11 over all species:

$$\rho_c v_c = \rho_g v_g \tag{12}$$

3.1.2.2 Energy Conservation. The interface equation of energy conservation is readily obtained from Eq. 9 by dropping the $\partial p/\partial t$ term, integrating across the boundary, and setting the net accumulation to zero. The resulting equation is

$$\rho_c v_c H_c + q_c = \rho_g v_g H_g + q_g \tag{13}$$

which indicates that convective enthalpy plus heat transport relative to hydrodynamic velocity is conserved across the interface.

3.2 CONSTITUTIVE EQUATIONS

Equations 6, 9, 11, and 13 cannot be solved as they stand because, when applied over all indicated species and relevant phases with appropriate initial and asymptotic conditions, there are more unknown quantities than equations. The required additional equations are provided by the transport relationships, the equation of state (taken for convenience as the perfect gas law), kinetic and stoichiometric expressions, and definitions.

3.2.1 Transport Relationships

The transport relationships express fluxes in terms of forces (gradients of physical quantities such as concentration, enthalpy, pressure, and velocity). A fundamental postulate of the thermodynamics of irreversible processes is that, for systems not far removed from equilibrium, the fluxes are linear homogeneous functions of the gradients. Expressions of higher degree would in general be required for large departures of the system from equilibrium; however, little work has been done on the higher order theories. Experimental results have confirmed the adequacy of the linear relationships over a wide range of conditions.

In the absence of viscous forces, the fluxes to be considered are mass and energy. The forces involved are related to gradients of pressure, temperature, and concentration. In the present analysis, only the direct effects are considered: the effects of pressure gradient on mass flux, of temperature gradient on mass flux (thermal diffusion or Soret effect), of external forces on mass flux (forced diffusion), and of concentration gradient on energy flux (Dufour effect) are neglected. The Soret effect is the most significant under ignition conditions but, even so, it probably contributes a maximum of only 10% of the total mass flux. With these simplifications, the energy and mass fluxes for a multi-component system are given by

$$q = -\lambda \frac{\partial T}{\partial x} + \Sigma j_i H_i + q_r \tag{14}$$

and

$$j_i = \frac{c^2}{\rho} \sum_{j=1,\, j\neq i}^{n} \mu_i \mu_j D_{ij} \frac{\partial x_j}{\partial x} \tag{15}$$

In Eq. 14, the three terms on the right express energy flux due to normal thermal conduction, diffusing species, and radiation, all relative to the barycentric velocity v. Equation 15 is obtained[7] from a more general expression by assuming the perfect gas law. It is seen that for a multicomponent system, the mass diffusion fluxes of the individual species are complicated functions of the concentration gradients of all the species. The multicomponent diffusion coefficients, D_{ij}, are generally functions of all the concentrations. Equation 15 may be expressed in different form[6] by:

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[7] Bird, R. B. *Theory of Diffusion*, ADVANCE CHEM ENG, Vol. 1. New York, Academic Press, 1956, pp. 155-239.

$$\frac{1}{\rho}\sum_{j=1,\, j\neq i}^{n} \frac{Y_i j_j - Y_j j_i}{\mu_j \mathcal{D}_{ij}} = \sum_{j=1,\, j\neq i}^{n} \frac{Y_j \nabla Y_i - Y_i \nabla Y_j}{\mu_j} \tag{16}$$

Equation 16 represents a set of simultaneous equations relating the mass diffusion fluxes, the mass concentrations and the mass concentration gradients ∇Y. An advantage of Eq. 16 is that the binary diffusion coefficients $\mathcal{D}$ are nearly insensitive to concentration; disadvantages are that the fluxes are expressed implicitly and that $n(n-1)/2$ binary coefficients must be specified to solve the problem. This latter requirement greatly increases the number of quantities required for a parameter study; other investigations[8] have shown that often the principal trends of results may be adequately calculated by assuming all binary coefficients to be equal. With this assumption Eq. 15 or 16 may be reduced to the form used in this report

$$j_i = -\rho\mathcal{D}\nabla Y_i = -\rho\mathcal{D}\,\frac{\partial Y_i}{\partial x} \tag{17}$$

which is known as Fick's first law of diffusion. We note that the derivation of Eq. 17 does not depend upon the frequently made assumption of equal molecular weights of all species.

3.2.2 Kinetics and Stoichiometry.

The conservation equations contain terms representing rates of transformation of chemical species (k_i, k_{is} for bulk and surface reactions) and rates of mass evolution (manifested by the convective terms in the interface equations). Chemical transformations are complicated by multiple path, opposing, or consecutive reactions, details of which are not fully known in complex combustion processes. The assumptions regarding the kinetic laws which must be made in order to achieve tractability probably reflect the greatest area of uncertainty in the formulation of any ignition or combustion theory. It is convenient to assume that the rate controlling step at a given site in a kinetic process consists of a simple, single step, irreversible reaction with rate following an Arrhenius dependence on local temperature. The stoichiometry of the overall chemical change will not correspond to that given by the reaction mechanism if other faster reactions occur involving the same components. We now consider the kinetic expressions for the changes appearing in the conservation equations. The processes to be considered were enumerated in Section 2.

3.2.2.1 Gas Phase. The two gas phase reactions included in the formulation are:

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[8] Kendall R. M., R. A., Rindal and E. P. Bartlett. "A Multicomponent Boundary Layer Chemically Coupled to an Ablating Surface," AMER INST AERON ASTRONAUT J, Vol. 5, No. 6 (June 1967), pp. 1063-71.

$$\text{Reaction 7:}\quad [F] + b_2[O] = b_7[P] \tag{18}$$

$$\text{Reaction 8:}\quad [F] + b_4[O] = b_8[P] \tag{19}$$

Equation 18 represents reaction of gas phase fuel (pyrolyzed from solid) with oxidizer pyrolyzed from the solid phase. The b's are molar stoichiometric coefficients relative to fuel taken as one. Mechanistic reaction orders with respect to fuel and oxidizer are taken as F7 and O7, respectively. Equation 19, employing analogous notation, pertains to the reaction of pyrolyzed fuel with oxidizer originally present in the gas phase: reaction orders are denoted as F8 and O8. Mass balance considerations lead to:

$$\mu_1 + \mu_2 b_2 = \mu_7 b_7 \tag{20}$$

$$\mu_1 + \mu_4 b_4 = \mu_8 b_8 \tag{21}$$

where the μ's denote molecular weights, μ_1 referring to the pyrolyzed gaseous fuel. Applying the law of mass action of chemical kinetics[9] to Reactions 7 and 8, we may represent the mass source terms k_i (cf., Eq. 6) as:

$$\text{Gas phase fuel:}\quad k_1 = -\mu_1\left(r_7 + r_8\right) \tag{22}$$

$$\text{Gas phase oxidizer (pyrolyzed from solid):}\quad k_2 = -\mu_2 b_2 r_7 \tag{23}$$

$$\text{Gas phase oxidizer (initially in gas):}\quad k_4 = -\mu_4 b_4 r_8 \tag{24}$$

$$\text{Product of reaction 7:}\quad k_7 = \mu_7 b_7 r_7 \tag{25}$$

$$\text{Product of reaction 8:}\quad k_8 = \mu_8 b_8 r_8 \tag{26}$$

where

$$r_7 = \nu_7\left(\rho_g Y_1/\mu_1\right)^{F7}\left(\rho_g Y_2/\mu_2\right)^{O7}\exp\left(-E_7/RT\right) \tag{27}$$

$$r_8 = \nu_8\left(\rho_g Y_1/\mu_1\right)^{F8}\left(\rho_g Y_4/\mu_4\right)^{O8}\exp\left(-E_8/RT\right) \tag{28}$$

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[9] Williams, F. A. *Combustion Theory*. Palo Alto, Ca., Addison-Wesley Pub. Co., 1965, 447 pp.

and where ν and E represent pre-exponential factor and activation energy of the appropriate reaction. Negative signs in the expressions for k indicate disappearance of the relevant species. Species 3, 5, 6, and 9 are not generated by gaseous reaction; consequently, their corresponding k's are zero.

3.2.2.2 Solid Phase. Reaction kinetics in the solid phase are more complicated than in the gas phase. The components of a solid are not completely mobile as is the case for a gas; instead, individual molecules are constrained to move relatively small distance within crystal lattices or across interfaces separating different constituents. Since each molecule does not have equal probability of collision with every other molecule, the usual method used in deriving rate expressions for gases cannot be employed. Therefore, solid phase reactions may be expected to depend upon first order decompositions or upon reactions which occur at internal interfaces. In the latter case, the question of reaction rate cannot be resolved without reference to geometrical considerations. Even the extent to which the reaction can proceed is limited by the diffusion rates of the solid reactants through films of products built up at the interfaces. It is clear from discussions presented in the literature[10,11] that no universally applicable rate theory is available and that topochemical considerations would be required to provide an accurate description of the solid phase process. However, the general aspects of solid phase reactions can be expressed by assuming reaction orders ranging from zero to two. Moreover, it has been shown[12] that, insofar as ignition is concerned, the thermal history of a solid undergoing bulk reaction is relatively insensitive to the kinetic order assumed. For simplicity in the present analysis, the following assumptions are made: (1) the kinetics is zero order, and (2) the solid phase composition can be characterized by a fuel-to-oxidizer ratio (even for homogeneous double-base propellants). Assumption (1) requires that careful account be kept of the amount of reactant consumed to prevent the physically unrealistic and numerically erroneous introduction of negative concentrations during computations. The single solid phase reaction is assumed to be

$$\text{Reaction 10:} \quad [F] + b_{11}[O] = b_{12}[P] \tag{29}$$

with the product [P] considered as inert, or the reverse reaction:

$$b_{12}[P] = [F] + b_{11}[O] \tag{30}$$

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[10] Cordes, Herman F. "The Preexponential Factors for Solid-State Thermal Decomposition," J CHEM PHYS, Vol. 72, No. 6 (June 1968), pp. 2185-89.

[11] Garner, W. E., ed. *Chemistry of the Solid State*. London, Butterworths, 1955.

[12] Bradley, H. H., Jr. "Theory of Ignition of a Reactive Solid by Constant Energy Flux," COMBUS SCI AND TECH, Vol. 2, No. 1 (August 1970), pp. 11-20.

representing the bulk phase dissociation into active fuel and oxidizer. Mass balance yields

$$\mu_{10} + \mu_{11} b_{11} = \mu_{12} b_{12} \tag{31}$$

and the source terms for reaction 10 (Eq. 6) are given by

$$k_{10} = -\mu_{10} r_{10} \tag{32}$$

$$k_{11} = -\mu_{11} b_{11} r_{10} \tag{33}$$

$$k_{12} = \mu_{12} b_{12} r_{10} \tag{34}$$

The rate r_{10} is given by

$$r_{10} = \nu_1 \, exp\left(-E_1/RT\right) \tag{35}$$

where E_1 is the activation energy of the solid reaction. The reverse process may be readily simulated by changing the signs of the expressions for the k's in Eq. 32-34 or of ν_1 in Eq. 35.

3.2.2.3 Interfacial Processes. The boundary between solid and gas phases may be the site of chemical transformations or of phase changes involving either simple gasification or dissociation. Rates of chemical transformation at the interface depend upon adsorption and desorption processes. Details of surface phenomena are discussed in the literature[9] (see p. 382 et. seq.); the results may be summarized by the statement that the apparent order of the reaction can vary between zero and the true kinetic order and may be of order minus one relative to the reaction product. The latter occurs when the product is strongly absorbed, thereby inhibiting the adsorption of additional reactants. The surface reactions considered in this analysis are: (1) reaction of pyrolyzed oxidizer with solid fuel and (2) reaction of original oxidizer from the gas phase with solid fuel. They are represented, respectively, by the following stoichiometries:

$$\text{Reaction 5:} \quad [F] + b_2'[O] = b_5[P] \tag{36}$$

$$\text{Reaction 6:} \quad [F] + b_4'[O] = b_6[P] \tag{37}$$

Corresponding to reactions 5 and 6, we have

$$\mu_{10} + \mu_2 b_2' = \mu_5 b_5 \tag{38}$$

$$\mu_{10} + \mu_4 b_4' = \mu_6 b_6 \tag{39}$$

The fuel mass consumption rates for the above are given by:

$$m_5 = \rho_c Y_{10} \nu_5 \left(\rho_g Y_2/\mu_2\right)^{S5} \exp\left(-E_5/RT_s\right) \tag{40}$$

$$m_6 = \rho_c Y_{10} \nu_6 \left(\rho_g Y_4/\mu_4\right)^{S6} \exp\left(-E_6/RT_s\right) \tag{41}$$

It is assumed that the surface rates are first order with respect to the fuel (proportional to fuel surface area) and of order S5 and S6 with respect to the pyrolyzed or initial oxidizer.

Ingredients subject to surface pyrolysis include initial solid fuel and oxidizer together with their solid phase reaction products, if any. The rates of pyrolysis may be controlled by an Arrhenius temperature expression or may proceed by an equilibrium vaporization process in which the gas phase equilibrium vapor pressure, hence mole or mass fraction, is related to total applied pressure and surface temperature. Combinations of the two processes lead to intermediate results. The assumption of surface rate controlling processes leads to more loosely coupled boundary conditions and is adopted here for reasons of mathematical simplicity. A brief description for the case where at least one equilibrium process is involved is presented in Appendix A. The mass fluxes of the solid phase fuel, oxidizer, and product are given for $i = 10, 11,$ and 12, respectively, by:

$$m_i = \rho_c Y_{cis} \nu_i \exp\left(-E_i/RT_s\right) \tag{42}$$

where fractional surface area of ingredient i has been set equal to its mass fraction. The values of Y_{cis} depend in general upon the initial composition of the solid phase and the extent of solid phase reaction and so depend upon a solution of the solid phase equations.

The rigorous application of Eq. 39-42 involves consideration of the changing topology of a heterogeneous surface. The complication is brought about by the fact that, unless the kinetic parameters and surface areas of the different components are uniquely related, each component must burn at a different linear rate, a conclusion which violates the assumption of one dimensionality. In steady state burning, it has been speculated that each component burns at a different temperature[13] but this explanation is not universally accepted. Actually, it is known that in steady state, each component burns at a different rate, with the surface topology adjusting itself to give areas necessary to accommodate equilibrium mass ratios typical of the solid. Further discussion to resolve the problem does not seem appropriate at present. The simplifying assumption is therefore made that each component of the propellant regresses at a rate consistent with the kinetic equation; the degree of departure of the surface from planar can then be partially assessed by examining the total regression of each component at the time of ignition and comparing differences with reasonable particle sizes. If such a test reveals that the surface has indeed become two-dimensional, then a two-dimensional analysis must be made or the alternate assumption adopted that the regression rate of the fastest burning component governs the overall regression rate. In addition, it is assumed for convenience that no solid, unreacted material is ejected from the surface to contribute a thermal effect in the gas phase. It should be noted that in no one-dimensional analysis is it possible to consider mechanistically the changing surface topology together with associated changes in surface areas of the components.

3.2.3 Radiant Energy Transfer

Except under hypergolic conditions at ambient temperatures, some sort of external energy source serves as the ignition stimulus in ignition experiments. Ordinarily this consists of a radiation source (laser, xenon arc, or carbon arc) focused onto the surface of the sample to be tested. The fractions of this flux which are absorbed and reflected depend upon the optical properties of the surface and of the bulk solid phase. Absorption may be confined to the surface for a completely opaque material or one with an absorbing agent applied to the surface. On the other hand, the energy may be deposited instantaneously in depth for a transluscent material, with attenuation being adequately described by an exponential relationship between flux density and distance (Beer's Law). With the passage of time, gases evolved from the surface processes commence to attenuate the incident energy beam. Again, if re-radiation by the gases is not appreciable, exponential decay of intensity is a reasonable approximation. This attenuation of the incoming stimulus by the evolved gases adds energy to the gas phase while denying it to the heated surface. As the temperature of the gas phase rises, re-radiation by the gases also begins to intervene. All these phenomena are complicated by being wavelength and species dependent, with gaseous absorption of reflected energy also playing a role of some importance. The principal effect investigated here

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[13] Schultz, R., and L. Green, Jr. *Third AGARD Colloquium*, Pergamon Press, 1958. "Studies of the Decomposition Mechanism, Erosive Burning, Sonance, and Resonance, for Solid Composite Propellants, in Combustion and Propulsion," pp. 367-420.

is the absorption of energy by the solid. It is assumed that incident flux density is spatially and temporally constant, and that the surface reflectivity remains constant during the heating phase. A simplified analysis of the inclusion of gas phase energy attenuation is presented in Appendix B.

3.2.4 Relationship of Enthalpy to Temperature

In the foregoing sections, the energy equation has been presented in terms of total enthalpy while reaction rates involve temperature, which is related to the thermal enthalpy. The general relationship between the temperature and total enthalpy is

$$H = \Sigma Y_i H_i = \Sigma Y_i \left(h_i^r + \int_{T_r}^{T} C_i \, dT \right) \tag{43}$$

where h_i^r is the chemical enthalpy of species i at some arbitrary reference temperature T_r. One convention, adopted here, is to assign zero enthalpy to the elements at T_r, so that h_i^r is the heat attending the formation at T_r of species i from the elements.

3.3 GOVERNING EQUATIONS

The relationships presented in Section 3.1 and 3.2 describe the phenomenon of solid propellant ignition completely, subject to the limitations mentioned. Owing to the nonlinear nature of the equations, exact analytic solutions have not been found; recourse must be to numerical methods or to one of several available approximate analytic techniques. A desirable resolution of the problem would be the application of both approaches and comparison of results; however, only the numerical method is to be employed in the current report.

While numerical analogs may be developed for the equations of Sections 3.1 and 3.2 as they stand, it is more convenient to combine some of them, to apply certain mathematical transformations, and to make additional simplifications in the interest of reducing the number of physical quantities to be subjected to a parameter study.

3.3.1 Species Conservation

Equations 6 and 17 may be combined directly to give a single equation describing the time and space distribution of each species. For the gas phase ($i = 1, 2 \ldots 9;\ x \geq 0$) the result is

$$\rho_g \frac{dY_i}{dt} = \frac{\partial}{\partial x}\left(\rho_g D \frac{\partial Y_i}{\partial x} \right) + k_i \tag{44}$$

In the solid phase ($i = 10, 11, 12$ $x \leq 0$) where the mass diffusion is negligible, the species balances are

$$\rho_c \frac{dY_i}{dt} = k_i \tag{45}$$

Equation 11, applied to each species, yields the following interface conservation laws:

Fuel:

$$m_{10} = m_s Y_1 - \rho_g D \frac{\partial Y_1}{\partial x} \tag{46}$$

Solid oxidizer:

$$m_{11} = m_s Y_2 - \rho_g D \frac{\partial Y_2}{\partial x} + \frac{\mu_2}{\mu_{10}} b_2' m_5 \tag{47}$$

Solid product:

$$m_{12} = m_s Y_3 - \rho_g D \frac{\partial Y_3}{\partial x} \tag{48}$$

Gaseous oxidizer:

$$0 = m_s Y_4 - \rho_g D \frac{\partial Y_4}{\partial x} + \frac{\mu_4}{\mu_{10}} b_4' m_6 \tag{49}$$

Product of surface reaction of fuel with pyrolyzed oxidizer:

$$0 = m_s Y_5 - \rho_g D \frac{\partial Y_5}{\partial x} - \frac{\mu_5}{\mu_{10}} b_5 m_5 \tag{50}$$

Product of surface reaction of fuel with gaseous oxidizer:

$$0 = m_s Y_6 - \rho_g D \frac{\partial Y_6}{\partial x} - \frac{\mu_6}{\mu_{10}} b_6 m_6 \tag{51}$$

Product of gaseous reaction of fuel with pyrolyzed oxidizer:

$$0 = m_s Y_7 - \rho_g D \frac{\partial Y_7}{\partial x} \tag{52}$$

Product of gaseous reaction of fuel with gaseous oxidizer:

$$0 = m_s Y_8 - \rho_g D \frac{\partial Y_8}{\partial x} \tag{53}$$

Inert gas:

$$0 = m_s Y_9 - \rho_g D \frac{\partial Y_9}{\partial x} \tag{54}$$

Equation (46) deserves special comment. Although the total mass flux of fuel contributing to m_{cis} in Eq. 11 includes m_5, m_6, and m_{10}, the reaction terms m_5 and m_6 are exactly cancelled by k_{is}. The quantity m_s in Eq. 46-54 represents the sum of all mass transferred across the boundary so that

$$m_s = m_5 + m_6 + m_{10} + m_{11} + m_{12} \tag{55}$$

The gaseous convection term in each surface conservation equation is represented by $m_s Y_i$, where the one-dimensional assumption of complete mixing of gaseous species at the surface has been made.

3.3.2 Energy conservation

If we assume specific heats are independent of temperature, it is possible to combine Eq. 6, 9, 14, 17, and 43 to obtain the following equation for thermal enthalpy h:

$$\overset{I}{\rho \frac{dh}{dt}} = \overset{II}{\frac{\partial}{\partial x} \left\{ \frac{\lambda}{C_{av}} \left[\frac{\partial h}{\partial x} + (Le - 1) \Sigma h_i \frac{\partial Y_i}{\partial x} \right] \right\}} - \overset{III}{\Sigma h_i^r k_i} + \overset{IV}{\beta q_{rs} \exp (\beta x)} \tag{56}$$

where

$$h_i = C_i \left(T - T_r \right) \tag{57}$$

$$h = C_{av} \left(T - T_r \right) \tag{58}$$

$$Le = \rho C_{av} D / \lambda \tag{59}$$

$$C_{av} = \Sigma C_i Y_i \tag{60}$$

The terms in Eq. 56 have the following physical interpretations:

I Thermal energy accumulation in a moving volume element

II Thermal energy added to volume element by differential processes

III Chemical energy generated, alternately represented by $\mu_r \Sigma Q_j r_j$,

where Q_j and r_j are the exothermicity and rate of the jth reaction with Q_j evaluated at the reference temperature. The factor μ_r is the molecular weight of the ingredient with respect to which heat effects are computed.

IV Radiant energy deposited in depth for the solid phase. The analogous term is discussed in Appendix B for the gas phase.

The portion of the diffusional term containing $Le-1$ as a factor accounts for two phenomena:

(1) difference in diffusional rates of mass and energy

(2) difference in specific heats of reactants and products

It is important to note that in the chemical energy term, the reaction rate k_i is taken at the instantaneous local temperature while the heat effect is related to the reference temperature. The fact that heat of reaction is generally temperature dependent is associated with the term containing $Le-1$ as a factor. In the interest of mathematical simplicity, we shall simplify Eq. 56 by the single assumption of equal specific heats for all species. This is tantamount to assuming a heat of reaction which is large compared with sensible heats over the range of temperature involved. The assumption of unity Lewis number is then unnecessary as the expression $h_i \, \partial Y_i/\partial x$ vanishes. Moreover, C_{av} becomes constant, thereby further simplifying the ensuing numerical procedures. The major effect of Lewis number still appears in Eq. 44 and in the mass interface conditions when $\rho_g \mathcal{D}$ is replaced by its equivalent from Eq. 59. The effects of different specific heats may be studied, if desired by using Eq. 56 as a point of departure and considering C_{av} as a function of x, thereby introducing local values of Y_i and $\partial Y_i/\partial x$ into Eq. 56.

The boundary condition for the energy equation is formulated by combining Eq. 13, 14, 17, and 43, with the assumption of equal specific heats for both phases. This latter step is equivalent to assuming that surface heat effects (chemical reaction and phase changes) are large compared with changes of sensible enthalpy. The final equation is

$$\frac{\lambda_c}{C_c}\frac{\partial h_c}{\partial x} = \frac{\lambda_g}{C_g}\frac{\partial h_g}{\partial x} + q_r + q_s \qquad (61)$$

Although apparently inconsistent with the above assumption, unequal specific heats are retained for the terms of the two phases in Eq. 61 because unequal specific heats represent only a second order effect on q_s, the surface heat release term, whereas the specific heat is a first order effect in the terms for conductive energy transport. The term q_r is the radiant heat absorbed at the mathematical interface. This thermal contribution is included either in Eq. 56 when β is finite or in Eq. 61 when β is infinite, but not in both.* The surface heating q_s is given by

$$q_s = m_5 Q_5 + m_6 Q_6 + m_{10} Q_{10} + m_{11} Q_{11} + m_{12} Q_{12} \tag{62}$$

in which the five Q's are the exothermicities accompanying the various surface changes (see Section 3.2.2.3).

3.3.3 Auxiliary Conditions

To complete the system of field and interface equations, initial conditions and conditions in each phase remote from the interface are prescribed.

Initial Conditions:

Solid:

$T_c\ (x,0) = T_{co}$

Fuel: $Y_{10}\ (x,0) = Y_{fc}$

Oxidizer: $Y_{11}\ (x,0) = 1 - Y_{fc}$

Product: $Y_{12}\ (x,0) = 0$

Gas:

$T_g\ (x,0) = T_{go}$

Oxidizer: $Y_8\ (x,0) = 1 - Y_{og}$

Inert: $Y_9\ (x,0) = 1 - Y_{og}$

All other $Y_i (i = 1\text{-}9) = 0$

Remote Conditions: Gradients of all quantities vanish at $x = -\infty$ for the solid phase and at $x = \infty$ for the gas phase.

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* Mathematically, as β approaches infinity, the behavior of the solution of the equations is as if the radiation term disappeared from the field equation and appeared in the boundary condition. Finite difference methods fail to realize this, however, and the dual treatment becomes necessary because of limitations of computers to the representation of finite quantities.

4. MANIPULATION OF EQUATIONS

The foregoing sections have been devoted to the development of the fundamental equations of a unified ignition theory. Presented in their physical form they are valuable in understanding the details of the physical processes involved; however, appropriate modifications are needed to convert the equations to a more convenient form for computational use. In general, these include non-dimensionalization through the use of characteristic quantities and coordinate transformations such as the use of similarity variables and stretching parameters. The equations at hand reprsent such a diversity of physical phenomena that there is no single set of characteristic quantities which apply in general. The resolution of this problem will be to delay the normalization procedure until a particular subcase of the unified theory has been chosen for study. In this way we retain flexibility while avoiding the choice of a characteristic quantity whose value may approach a limit of zero or infinity. Similarity transformations have not yet been found for the type of equation involving an exponential nonlinearity in the dependent variable. This section will present the two coordinate transformations used to convert the equations for computational use.

4.1 HOWARTH TRANSFORMATION

The substantial or total derivatives which appear in Eq. 44, 45, and 56 contain the local phase velocity implicitly (see Eq. 6 and 9). Owing to the constant pressure approximation of the momentum equation, only the global continuity equation remains as an independent relation containing the local velocity. Let us define

$$\psi = \int_0^x \frac{\rho}{\rho_0}\, dx \tag{63}$$

with ρ_0 taken as some reference (here initial) value of ρ whence

$$\frac{\partial \psi}{\partial t} = \int_0^x \frac{1}{\rho_0} \left(\frac{\partial \rho}{\partial t}\right) dx = -\int_0^x \frac{1}{\rho_0} \frac{\partial (\rho v)}{\partial x}\, dx = -\frac{1}{\rho_0}\left[(\rho v) - (\rho v)_s\right] \tag{64}$$

and

$$\frac{\partial \psi}{\partial x} = \frac{\rho}{\rho_0} \tag{65}$$

or

$$\frac{\partial}{\partial x} = \frac{\rho}{\rho_o}\frac{\partial}{\partial \psi} \qquad (66)$$

Then using the following standard rules of partial differentiation:

$$\left(\frac{\partial}{\partial t}\right)_\psi = \left(\frac{\partial}{\partial t}\right)_x + \left(\frac{\partial x}{\partial t}\right)_\psi \left(\frac{\partial}{\partial x}\right)_t \qquad (67)$$

$$\left(\frac{\partial x}{\partial t}\right)_\psi = -\left(\frac{\partial \psi}{\partial t}\right)_x \Big/ \left(\frac{\partial \psi}{\partial x}\right)_t \qquad (68)$$

we may derive

$$\frac{d}{dt} = \frac{\dot{m}_s}{\rho_o}\left(\frac{\partial}{\partial \psi}\right)_t + \left(\frac{\partial}{\partial t}\right)_\psi \qquad (69)$$

Application of Eq. (66) and (69) to Eq. (44), (45) and (56) provides the following:

$$\frac{\partial Y_i}{\partial t} = -\frac{\dot{m}_s}{\rho_o}\frac{\partial Y_i}{\partial \psi} + \frac{1}{\rho_o^{\,2}}\frac{\partial}{\partial \psi}\left(\rho^2 D\,\frac{\partial Y_i}{\partial \psi}\right) + \frac{k_i}{\rho} \qquad (70)$$

$$\frac{\partial h}{\partial t} = -\frac{\dot{m}_s}{\rho_o}\frac{\partial h}{\partial \psi} + \frac{1}{\rho_o^{\,2}}\frac{\partial}{\partial \psi}\left(\frac{\rho\lambda}{c}\frac{\partial h}{\partial \psi}\right) + \frac{\ddot{w}_r}{\rho}\,\Sigma Q_f r_j + \frac{\beta}{\rho}\,\dot{q}_r \exp\left(\rho_o \frac{\beta}{\rho}\,\psi\right) \qquad (71)$$

The interface Eq. 46-54 are not greatly changed except that the diffusion terms become

$$\rho_g^{\,2}\,D\partial Y_i/\partial \psi$$

In Eq. 71 the term involving Lewis number has been eliminated for reasons previously discussed (see Section 3.3.2). The final term of Eq. 71 would appear only for the solid phase and for finite β. Equation 70 applies to the solid phase with D set to zero.

Results of using the Howarth transformation are:

(1) The global equation of continuity is satisfied identically in the transform space. As a result the set of Eq. 70 contains one redundant equation of each phase. This redundancy is retained in the numerical analysis to provide an accuracy check.

(2) The coefficient of the convective term $(\partial/\partial\phi)$ is not a function of position but depends only upon the instantaneous value of m_g, the total rate of mass transfer across the interface.

(3) The coefficients appearing in the diffusion terms, i.e., $\rho\lambda/c$ and $\rho^2 \mathcal{D}$, are more nearly independent of temperature for a given pressure than are their counterparts in the untransformed equations; hence, they may be moved outside the partial differential operator.

A disadvantage of Howarth transformation is the need to perform the inverse (integral) transformation

$$x = \rho_o \int_o^{\psi} \frac{d\psi}{\rho} = \frac{\rho_o}{\alpha} \int_o^{\phi} \frac{d\phi}{(1 \pm \phi)\rho(\phi)} \tag{72}$$

in order to recover the true distance scale. If the surface conditions are all that are required, this extra step is eliminated.

4.2 TRANSFORMATION FROM INFINITE TO FINITE DOMAIN

The extent of the space scale ranges from minus to plus infinity. However, computer simulation by finite differences can deal only with finite quantities. One way out of the difficulty is to repeat the computional effort for several large finite values for the distance of the remote boundaries until the solutions converge.[14] The technique employed here is to use an exponential transformation of the distance scale which has the added feature of providing closer spacing of space nodes near the interface where gradients are larger. The transformation relationships are

$$\phi_c = -1 + \exp\left(\alpha_c \psi_c\right) \tag{73}$$

$$\frac{\partial}{\partial\psi_c} = \alpha_c \left(1 + \phi_c\right) \frac{\partial}{\partial\phi_c} \tag{74}$$

$$\frac{\partial^2}{\partial{\psi_c}^2} = {\alpha_c}^2 \left(1 + \phi_c\right)\left[\left(1 + \phi_c\right)\frac{\partial^2}{\partial{\phi_c}^2} + \frac{\partial}{\partial\phi_c}\right] \tag{75}$$

for the solid phase $(-1 < \phi_c < 0)$

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[14] Naval Weapons Center. *Theory of Ignition of A Reactive Solid by Constant Energy Flux*, by H. H. Bradley, Jr., China Lake, Calif., NWC, November 1968. 44 pp. (NWC TP 4618).

and

$$\phi_g = 1 - exp\left(-\alpha_g \psi_g\right) \tag{76}$$

$$\frac{\partial}{\partial \psi_g} = \alpha_g\left(1-\phi_g\right)\frac{\partial}{\partial \phi_g} \tag{77}$$

$$\frac{\partial^2}{\partial {\psi_g}^2} = {\alpha_g}^2\left(1-\phi_g\right)\left[\left(1-\phi_g\right)\frac{\partial^2}{\partial {\phi_g}^2} - \frac{\partial}{\partial \phi_g}\right] \tag{78}$$

for the gas phase $(0 < \phi_g < 1)$.

Application of Eq. 73–78 yields the final transformed equations to be solved numerically:

$$\frac{\partial z_i}{\partial t} = A_i B_i (1 \pm \phi)^2 \frac{\partial^2 z_i}{\partial \phi^2} - A_i (1 \pm \phi)\left(m_s \mp B_i\right)\frac{\partial z_i}{\partial \phi} + V_i \qquad (i = 1\text{-}14) \tag{79}$$

with initial conditions

$$z_i(\phi,\ 0) = z_{io} \qquad (i = 1\text{-}14) \tag{80}$$

and remote boundary conditions

$$\frac{\partial z_i}{\partial \phi}(\mp 1,\ t) = 0 \qquad \begin{array}{l} i = 1\text{-}9,\ 13 \ \ gas \\ i = 10\text{-}12,\ 14 \ \ solid \end{array} \tag{81}$$

Interface boundary conditions for species are given by

$$m_{i+9} = m_s z_i - B_i \frac{\partial z_i}{\partial \phi} - S_i \qquad (i = 1\text{-}9) \tag{82}$$

with the left hand side defined as zero for $i > 3$

and for energy by

$$B_{14}\frac{\partial z_{14}}{\partial \phi} = B_{13}\frac{\partial z_{13}}{\partial \phi} + S_{1314} \tag{83}$$

where S_{1314} is the surface energy source.

In Eq. 79-83 the symbol Z represents a general dependent variable, either mass or energy in either the solid or gas phase. The upper and lower signs correspond to solid and gas phase, respectively. Volumetric and surface sources are denoted by V and S, respectively. Other details regarding the symbols are indicated in the table of nomenclature.

Appendix A

INTERFACE CONDITIONS FOR EQUILIBRIUM PYROLYSIS OF ONE OR MORE SOLID PHASE CONSTITUENTS

The interface species mass balances for pyrolyzing species are provided by Eq. 46-48 for the case where all surface processes are controlled by Arrhenius type rate expressions. At the other extreme, the interface condition may include equilibrium transfers of one or more species in which the phase rule governs the relationship between concentration, pressure, and temperature. Consider, for example, the case of equilibrium transfer of ingredient 10 (solid fuel) while Arrhenius rate expressions govern the solid oxidizer and product surface conditions. We have then for the balance of fuel:

$$m_{10} = m_s Y_1 - \rho_g D \frac{\partial Y_1}{\partial x} \tag{A-1}$$

which may be rewritten as

$$m_{10} = (\Sigma m) Y_1 + m_{10} Y_1 - \rho_g D \frac{\partial Y_1}{\partial x} \tag{A-2}$$

In Eq. A-2, m_s has been replaced by $\Sigma m + m_{10}$, the summation being taken over all species except the one in question (fuel in this case). The mass fraction Y_1 (a function of mole fraction and molecular weight of all species) is determined, for equilibrium processes, by total pressure and surface temperature through the Clausius-Clapeyron relationship. If fuel is the only component undergoing an equilibrium phase change, all the terms in Σm depend on rate expressions and may be evaluated from surface temperature and composition. If more than one equilibrium process occurs, a relation analogous to Eq. A-2 applies for each process, leading to a set of simultaneous boundary conditions. In the present theoretical analysis and its associated computer program, equilibrium processes are not considered; the condition of constant surface temperature and concentration is not obtainable by a simplification of the general expressions unless convection and surface regression are neglected.

Appendix B

SIMPLIFIED ANALYSIS OF EFFECT OF ABSORPTION OF RADIANT ENERGY BY GAS PHASE SPECIES

The common assumption made in modeling solid propellant ignition by radiant flux is that the beam suffers no attenuation in passing from the source to the surface. Absorption of incoming energy by gaseous species has the dual effect of adding energy to the gas phase while partially blocking it from the propellant surface. Assuming that only the evolved gases contribute to energy absorption, that energy reflected from the surface is negligible, and that equal absorption coefficients apply, the gas phase energy equation is modified by addition of the term

$$\frac{\partial}{\partial x}\left[I_\infty \exp\left(-\int_x^\infty \beta_g \rho_g Y \, dx\right)\right] \tag{B-1}$$

In Eq. B-1, I_∞ represents the unattenuated source flux while Y is the sum of all species produced by any chemical or physical transformation; hence, $Y = 1-Y_4 - Y_9$.

We may write

$$-\int_x^\infty \rho_g Y \, dx = -\int_0^\infty \rho_g Y \, dx + \int_0^x \rho_g Y \, dx \tag{B-2}$$

Also, it is noted that all new species must ultimately originate at the surface, so that at time t

$$\int_0^\infty \rho_g Y \, dx = \int_0^t m_s \, dt \tag{B-3}$$

Carrying out the differentiation of expression (B-1) leads to the addition of the term

$$q_{sg}\beta_g\rho_g Y(x)\ \exp\left[\int_0^x \beta_g\rho_g Y(x)\ dx\right] \qquad \text{(B-4)}$$

to Eq. 56. Here

$$q_{sg} = I_\infty \exp\left(-\int_0^t m_s\ dt\right) \qquad \text{(B-5)}$$

is the flux at the surface after attenuation by the entire gas column and the expression (B4) is the energy absorption by the gas at position x. Transformations into the ψ and ϕ coordinate systems lead to the additional terms

$$q_{sg}\beta_g Y\left(\psi_g\right)\ \exp\left[\int_0^\psi \beta_g\rho_{go} Y\left(\psi_g\right)\ d\psi\right] \qquad \text{(B-6)}$$

in the gas phase representation of Eq. 71 and

$$q_{sg}\beta_g Y\left(\phi_g\right)\left[\exp\int_0^{\phi_g}\left(\beta_g\rho_{go}/\alpha_g\right) Y d\phi_g/\left(1-\phi_g\right)\right] \qquad \text{(B-7)}$$

in Eq. 79.

The foregoing is a simplified analysis of an admittedly complex phenomenon. Expansion of the ideas to include other effects such as variable β_g and gas re-radiation would not be difficult in principle. The entire matter is usually neglected on physical grounds and in addition is omitted in the current study to avoid introduction of more complicated numerical analysis than appears warranted by probable gains.