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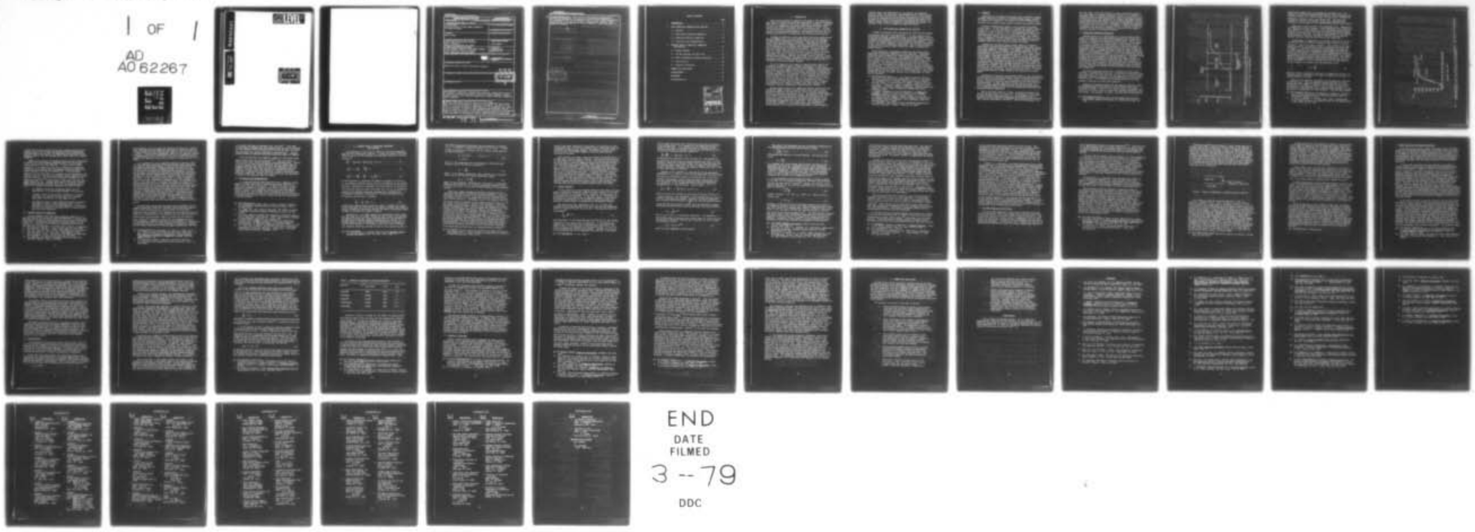

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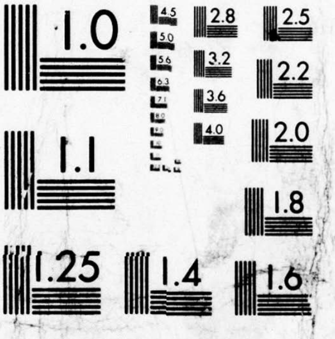

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A brief, qualitative review of some of the basic assumptions used in macroscopic models of solid-propellant combustion is presented. The intent of the review is to discuss the limits of applicability of the assumptions and, thereby, to isolate problems in combustion theory requiring more microscopic analysis. Special consideration is given to such problems as heat conduction in the burning propellant, phase transitions at the surface, characterization of the nonequilibrium environment in the material, and the effects of that environment upon — (over) chemical-reaction rates. Some relatively new theoretical techniques for analyzing the problems will be discussed, as well as some diagnostic techniques for experimental study and verification. Where possible, specific future investigations are recommended and possible benefits to combustion theory in general are explored.

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1. INTRODUCTION

Most existing studies of combustion are based on the assumption of the validity of models developed from experimental or empirical knowledge. When used in conjunction with various conservation equations, equations of state, and assumptions concerning global reaction kinetics, they theoretically predict information about the burning process. The goal of such theoretical investigations is to better understand the physical principles occurring during combustion and thereby to determine how the burning characteristics of propellants can be predicted and modified.

Although the theoretical basis upon which combustion studies depend has not changed much in the last twenty-five years, the development of sophisticated computational techniques during that time has made possible more detailed model calculations. Unfortunately, however, little effort has been expended to determine the applicability of many of the assumptions in the models under consideration or to determine when a more microscopic treatment is necessary. (By microscopic we mean here studies that must be carried out on the atomistic level.) Since the payoff resulting from microscopic studies tends to be rather long-range, the lack of attention to this aspect of the problem is perhaps understandable. However, the current state of the art is such that most of the fundamental information that can be gained from totally macroscopic models has been learned and the time is ripe for the investigation of more microscopic concepts.

It is the purpose of this report to examine briefly some of the fundamental assumptions made in commonly used models of combustion (and ignition) and to indicate possible shortcomings in these assumptions. In so doing, we will suggest various areas of chemistry and physics as applied to combustion which, in our opinion, need further investigation. Possible approaches to the treatment of these problems involving newly developed theoretical techniques will also be suggested and, to the extent possible at the present time, we will indicate how the results of the investigations can be included in the macroscopic models. In this regard, we should indicate that our intention is not to replace existing models but, rather, to augment them where necessary with information obtained independently from microscopic studies.

We shall begin in Sec. II by summarizing briefly some of the basic assumptions common to models currently used in the study of solid-propellant combustion and ignition and indicate the basic mechanisms by which the burning is believed to occur. The discussion will emphasize those aspects of the problem given further consideration in Sec. III. In Sec. III, we discuss critically the chemistry and physics of the combustion process, indicating the conditions under which we expect the prevalent assumptions to no longer hold. The discussion will include heat transport in the burning solid, phase transitions, characterization of the nonequilibrium environment in which chemical reactions occur, and modifications to the reaction-rate formalism necessary under such conditions. Some techniques for verifying experimentally and also treating theoretically these aspects of the problem will also be indicated as well as possible benefits from these studies. In order not to obscure the discussion with mathematical details, an effort is made to make the discussion as qualitative as possible. We conclude in Sec. IV with a summary and some conclusions.

2. SOLID-PROPELLANT COMBUSTION AND IGNITION

A number of excellent review articles exist which discuss problems of propellant ignition[1,2] and combustion[3-6]. In this section we will discuss only the barest essentials of some of the major models in order to provide some background for the ensuing discussion. The review is not intended to be detailed nor the list of references encyclopedic. Discussion will be limited primarily to those aspects of the theory discussed in Sec. 3 and will be completely qualitative. Most of the discussion is contained in the articles cited to which the reader is referred for further details.

Solid propellants are generally divided into two classes which depend upon the physical composition of the propellant. Double-base propellants consist primarily of nitrocellulose and some explosive material (usually nitroglycerin). Some additional materials, however, may be added to serve as burning-rate modifiers or stabilizers. Composite propellants consist of particles of solid oxidizer imbedded in a host material. The host material usually provides the fuel for the combustion reaction although solid reducing agents are also included in the compositions. In many ways, particularly with regard to microscopic aspects, the burning of double-base and composite propellants is similar[4] and the emphasis of this report will be on the former case. Most of the fundamental concepts discussed, however, will be applicable to either type of propellant.

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1. E.W. Price, H.H. Bradley, Jr., G.L. Dehoritz, and M.M. Ibiricu, "Theory of Ignition of Solid Propellants", AIAA J. 4, 1153 (1966).
2. A.G. Merzhanov and A.E. Averson, "The Present State of Thermal Ignition Theory: An Invited Review", Combust. Flame 16, 89 (1974).
3. R.L. Derr, D. Ewing and D. Baker, "Combustion Theories for Solid Propellants - a Review", Combustion Laboratory, Thermal Sciences and Propulsion Center, School of Mechanical Engineering, Purdue University, 1973.
4. C. Huggett, "Combustion of Solid Propellants", in Combustion Processes, edited by B. Lewis, R.N. Pease, and H.S. Taylor (Princeton University Press, Princeton, 1956), V. II, p. 514.
5. A.F. Belyaev and N.N. Bakhman, "Theory of Burning of Powders and Solid Rocket Propellants (Review)", FGV (Combustion, Explosion, and Shock Waves) 2, 3 (1966).
6. A.G. Merzhanov, "The Theory of Stable Homogeneous Combustion of Condensed Substances", Combust. Flame 13, 143 (1969).

2.1 Ignition.

Combustion is initiated by delivering to the propellant an amount of energy sufficient to initiate a self-sustaining chemical reaction. The energy can be imparted to the surface in several different ways, and three basic theories[1] have evolved to analyze the ignition process.

The most straightforward theory is the so-called solid-phase thermal theory. In this treatment it is assumed that thermal energy is transported to the propellant interior from the surrounding gas by conduction or from a radiant source. The temperature interior to the propellant surface rises until it is sufficiently high to initiate a self-sustaining chemical reaction in the solid phase. The "reaction rate" is assumed to increase exponentially with temperature as in the Arrhenius formalism. By use of such a term, one masks considerable ignorance about the actual chemical processes occurring.

Although the solid-phase thermal theory appears to represent qualitatively the ignition mechanism in some propellants, many, particularly some composite propellants, do not appear to undergo exothermic, solid-phase reactions. Furthermore, the ambient conditions of the surrounding gas are known to affect ignition and these effects are not accounted for in any of the solid-phase theories. As a result, there arose a number of gas-phase theories intended to include the above considerations. The basic characteristic of all the gas-phase theories is that the self-sustaining reaction occurs between fuel and oxidizer in the gas phase. The source of ignition arises from heat conducted from the hot, oxidizing gases (perhaps preheated by a shock wave) into the propellant surface. The heat then vaporizes the propellant and the resulting fuel vapors diffuse into the gas phase where they react with the oxidizing gas, effecting a self-sustaining heat source. In none of the gas-phase theories is heat assumed to be liberated in the solid phase.

In addition to the solid- and gas-phase theories, some consideration has been given to an ignition process in which the controlling reactions occur at the propellant surface. Such a theory evolved because propellant surfaces are known to react significantly with the surrounding oxidizing gases. In this "hypergolic" theory ignition occurs as a result of strong oxidizing gases reacting with the propellant surface in an Arrhenius fashion, giving rise to an exponential increase in the propellant-surface temperature.

None of the above theories is likely to describe completely the ignition mechanism under any conditions. Unfortunately, little effort has been directed toward subjecting a set of experimental data to analysis by various theories to determine which theory is more reliable under specific experimental conditions. Even more unfortunate is the fact that such a test would probably be rather inconclusive owing to the large number of adjustable parameters present in all theories. A noteworthy effort to combine the theories and allow ignition to occur by any or all of the above processes has recently been made by Bradley[7]. As he himself points out, however, it is virtually impossible to test quantitatively his unified theory since most of the physical quantities are not known with any accuracy. Furthermore, although the treatment is perhaps a *tour de force* in ignition theory, it employs without real justification the macroscopic assumptions, especially with regard to chemistry, present in the separate theories.

2.2 Double-Base Propellant Combustion.

Whereas ignition is a time-dependent or transient effect, most studies of combustion are based on the assumption that the process is steady in a reference frame that moves with the burning front. It is furthermore assumed (as in ignition) that the burning is a one-dimensional process, taking place along parallel layers (Piobert's law). To facilitate analysis it is most convenient to divide the region in which double-base-propellant combustion occurs into four separate and independent zones. A schematic diagram of the four zones is shown in Figure 1. The subsurface or foam zone includes in principle the entire region below the propellant surface. It is in this region that the decomposition of the nitrocellulose and nitroglycerin is initiated forming nitrogen dioxide and fragments of inorganic molecules. The heat necessary for the decomposition arises from that conducted back into the propellant from the burning surface and from that released as a result of the reaction process. The subsurface zone is also referred to as the foam zone, perhaps because minute bubbles of gas have been observed just below the surface in many propellants after the burning was extinguished.

The above discussion applies only to propellants which undergo exothermic, condensed-phase reactions. As pointed out previously, many solid propellants fall into this class but some, the so-called volatile substances, undergo a transition to a gas phase prior to the time the reactions occur. Such substances have burning characteristics very similar to the gases into which they vaporize[5].

Between the propellant surface and the luminous flame lies a dark or nonluminous region which actually consists of two of the zones indicated in Figure 1. Directly next to the surface lies the fizz zone in which it is believed that a second-order, gas-phase exothermic reaction occurs. The reactants, of course, are those which result from the

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[7] H.H. Bradley, "A Unified Theory of Solid Propellant Ignition", Naval Surface Weapons Center Report No. TP5618, China Lake, CA, 1974.

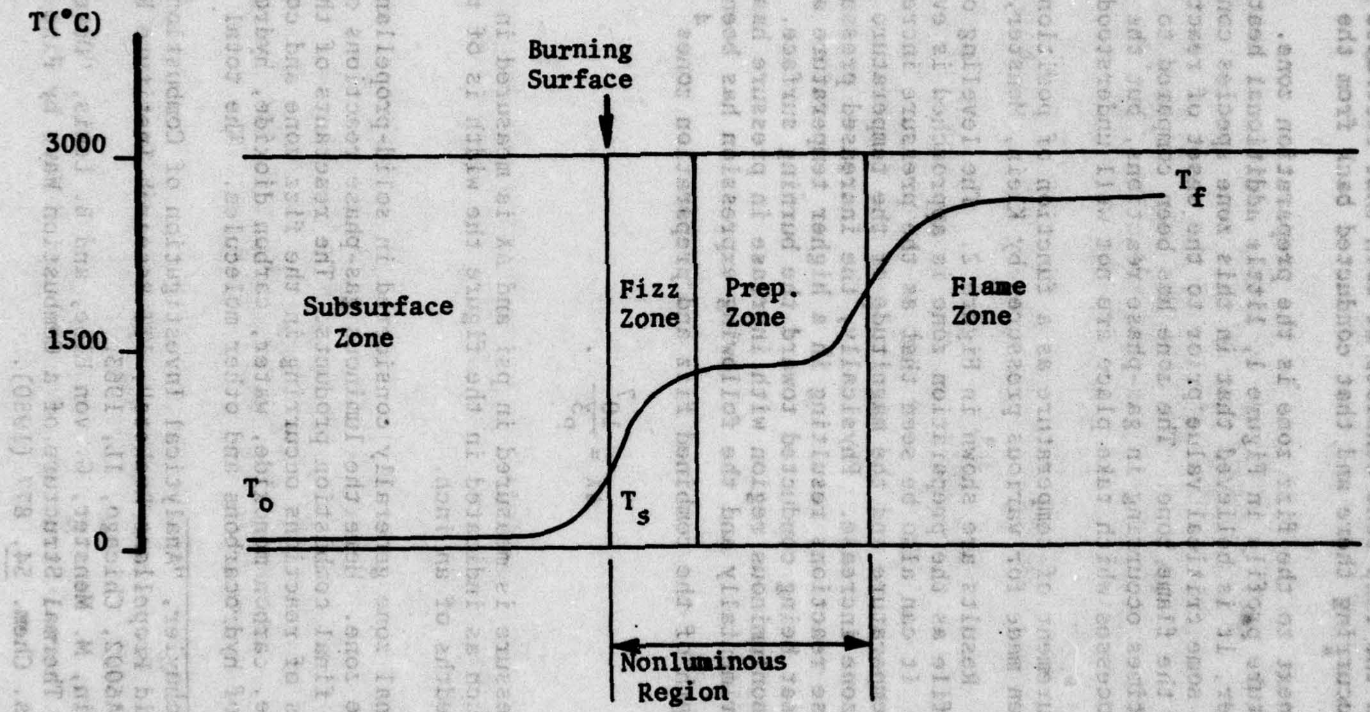

Fig. 1. Zones employed in the analysis of solid-propellant combustion. The temperature profile is that of a "typical" solid propellant. T_o is the ambient temperature, T_s that of the surface, and T_f the final flame temperature.

unimolecular decomposition in the propellant subsurface zone. The details of the reaction mechanism within the fizz zone are unknown, but reactions probably occur among nitrogen dioxide, glyoxal, formaldehyde, formic acid, hydrogen cyanide, and nitrous acid[8]. The total heat contained in the fizz zone consists of both that liberated by the reactions occurring there and that conducted back from the flame region.

Lying next to the fizz zone is the preparation zone. Judging from the temperature profile in Figure 1, little additional heat is liberated here. Rather, it is believed that in this zone species concentrations build up to some critical value prior to the onset of reactions characteristic of the flame zone. The zone has been compared to the induction period sometimes occurring in gas-phase reactions, but the detailed physical processes which take place are not well understood.

A measurement of temperature as a function of position in the fizz zone has been made for various pressures by Klein, Menster, von Elbe, and Lewis[9]. Results are shown in Figure 2. The leveling of the temperature profile as the preparation zone is approached is evident from the figure. It can also be seen that as the pressure increases both the final temperature and the magnitude of the temperature gradients within the zone increase. Physically, the increased pressure accelerates the gas-phase reactions resulting in a higher temperature and a larger amount of heat being conducted toward the burning surface. The shortening of the nonluminous region with increase in pressure has been observed experimentally and the following expression has been suggested for the length of the combined fizz and preparation zones[4]

$$\Delta X = \frac{10^7}{P^3} \quad . \tag{1}$$

Here the pressure is measured in psi and ΔX is measured in inches. For pressures such as indicated in the figure the width is of the order of a few hundredths of an inch.

The final zone generally considered in solid-propellant combustion is the flame zone. Here the luminous gas-phase reactions occur and produce the final combustion products. The reactants of this zone are the products of reactions occurring in the fizz zone and consist of nitric oxide, carbon monoxide, water, carbon dioxide, hydrogen, nitrogen and traces of hydrocarbons and other molecules. The total heat produced

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[8] F.L. Schuyler, "Analytical Investigation of Combustion Instability in Solid Propellant Rockets", ITT Research Institute Report No. IITRI-A6002, Chicago, IL, 1963.

[9] R. Klein, M. Menster, G. von Elbe, and B. Lewis, "Determination of the Thermal Structure of a Combustion Wave by Fine Thermocouples", J. Phys. Chem. 54, 877 (1950).

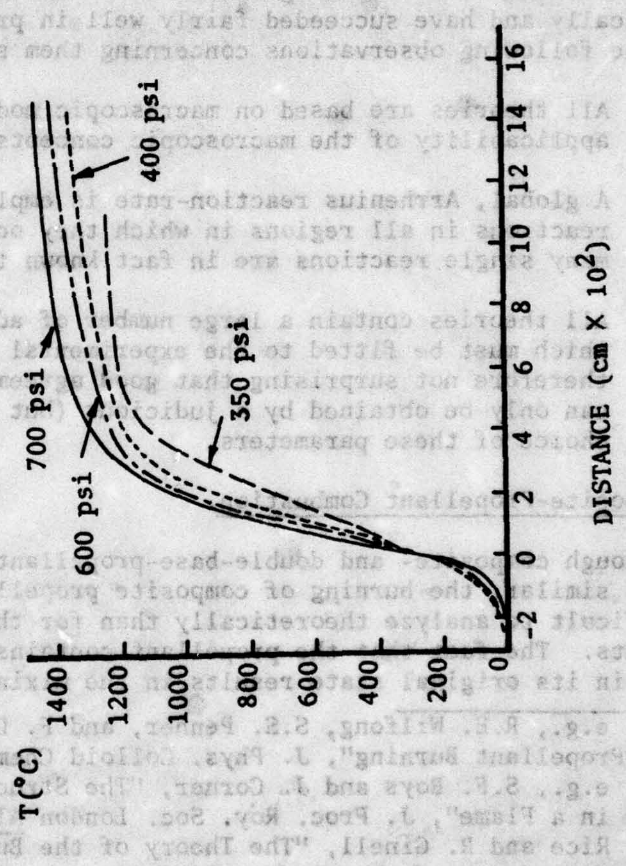

Fig. 2. Temperature profile near the surface of a burning propellant. Data are for nitrocellulose (13.15% Nitrogen) plus 1% ethyl centralite (from Ref. 9).

in this zone is about one-half of the total produced from the entire reaction process, but no detailed temperature profile measurements have been made in this region. The temperature of the final reacted products, however, has been measured and is about 2500°C for a typical propellant.

Theories for treating the combustion process can most conveniently be divided into three categories depending upon which of the four regions discussed above they emphasize. In the so-called surface theories[10], it is assumed that the rate of combustion is determined exclusively by the rate at which the unburned propellant beneath the surface undergoes unimolecular decomposition. In the gas-phase theories[11], on the other hand, it is assumed that the subsurface decomposition occurs at a rate just fast enough to supply reactants for the gas-phase reactions. By far the most successful treatments are the combination theories[12,13] which account in some detail for more than a single combustion zone. Although these theories are rather detailed mathematically and have succeeded fairly well in predicting burning rates, the following observations concerning them should be made:

1. All theories are based on macroscopic models and the applicability of the macroscopic concepts is not assessed.

2. A global, Arrhenius reaction-rate is employed to describe reactions in all regions in which they occur, although many single reactions are in fact known to occur.

3. All theories contain a large number of adjustable parameters which must be fitted to the experimental data. It is therefore not surprising that good agreement with experiment can only be obtained by a judicious (but by no means unique) choice of these parameters.

2.3 Composite-Propellant Combustion.

Although composite- and double-base-propellant combustion is in some ways similar, the burning of composite propellants is usually much more difficult to analyze theoretically than for the case of double-base propellants. The fact that the propellant contains unmixed fuel and oxidizer in its original state results in the mixing process itself

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[10] See, e.g., R.E. Wilfong, S.S. Penner, and F. Daniels, "An Hypothesis for Propellant Burning", J. Phys. Colloid Chem. 54, 863 (1950).

[11] See, e.g., S.F. Boys and J. Corner, "The Structure of the Reaction Zone in a Flame", J. Proc. Roy. Soc. London A197, 90 (1949).

[12] O.K. Rice and R. Ginell, "The Theory of the Burning of Double-Base Rocket Powders", J. Phys. Colloid Chem. 54, 885 (1950).

[13] D.B. Spalding, "The Theory of Burning of Solid and Liquid Propellants", Combust. Flame 4, 59 (1960).

being important, at least under some experimental conditions. Furthermore, the wide variety of composite types makes it rather unlikely that a single theory of composite-propellant combustion can cover the process in general. Finally, the inhomogeneous nature of the propellant produces an inhomogeneous surface and reaction zone, and the model developed to describe the combustion process must be capable of accounting for such an effect.

It is possible to analyze composite-propellant combustion using the same four zones discussed for the case of double-base propellants. For composite propellants, however, experiment has shown that the particular mode of combustion depends strongly on both the pressure and the size of the particles constituting the propellant. At very low pressures, the burning rate appears to be controlled primarily by the gas-phase reaction among products resulting from the solid-phase decomposition and the burning is very similar to that of a premixed gas flame. In this region the burning rate is strongly dependent on pressure and nearly independent of particle size. At very high pressures, on the other hand, the burning rate depends only weakly on both pressure and particle size. It appears that here the combustion is controlled by the rate at which fuel and oxidizer mix, no doubt because the reaction rates are very high at high pressures (above about 500 psi) and therefore the mixing rate becomes the limiting process. Finally, at intermediate values of the pressure, burning rates are dependent on both pressure and particle size. Experimental results suggest that in this regime the flame contains pockets of oxidizer gas released from the solid surface. The physical reason for the existence of such pockets is unknown. As might be expected burning rates are dependent upon both the interdiffusion and chemical-reaction rates[3].

No theory has thus far been developed which successfully explains composite-propellant combustion, although a number have been suggested which account qualitatively for various aspects of the process. Summerfield and coauthors[14] first suggested the idea that the propellant burned as a premixed flame at low pressures and as a diffusion flame at high pressures and developed a theory to account for this behavior. Later, Hermance[15] attempted to account for the inhomogeneous nature of the propellant surface by describing it statistically, a consideration that had been omitted in the early treatment of Summerfield. Probably the most widely used model for treating composite-propellant combustion

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[14] M. Summerfield, G.S. Sutherland, M.J. Webb, H.J. Tabak, and K.P. Hall, "Burning Mechanism of Ammonium Perchlorate Propellants", in ARS Progress in Astronautics and Rocketry: Solid Propellant Rocket Research, edited by M. Summerfield (Academic, New York, 1960), V. I, p. 141.

[15] C.E. Hermance, "A Model of Composite Propellant Combustion Including Surface Heterogeneity and Heat Generation", AIAA J. 4, 1629 (1966).

is the model developed by Beckstead, Derr, and Price[16]. This model was developed by assuming that the gas-phase reaction could be described by three separate flames surrounding each oxidizer particle, an assumption consistent with earlier experimental investigations[17]. The propellant surface was described using the statistical method of Hermance.

Since the BDP model was suggested, a number of other models along rather similar lines have been proposed[18-20]. Many can predict, at least in some cases, results consistent with experimental data. However, it is fair to say that the above-mentioned theories contain many adjustable parameters that must be fitted to the experimental data and agreement with experiment comes only after the parameters have been carefully selected. As we have pointed out, composite-propellant combustion is substantially more difficult to analyze than double-base-propellant combustion. Further work, both theoretical and experimental is needed in this difficult area of research.

2.4 Conclusions and Recommendations.

It is apparent from the above discussion that a complete, unified theory of either double-base-or composite-propellant combustion is likely to be very far in the future. In view of this fact, it would appear most worthwhile for workers in the field to isolate specific problems relevant to the combustion process and study them independently in detail. Only through such an undertaking can one hope to significantly advance the state of the art from our present capabilities. In the following section we outline a number of specific areas amenable to further research.

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16. M.W. Beckstead, R.L. Derr, and C.F. Price, "A Model of Composite Solid-Propellant Combustion Based on Multiple Flames", AIAA J. 8, 2200 (1970).
17. T.L. Boggs, R.L. Derr, and M.W. Beckstead, "The Surface Structure of Ammonium Perchlorate Composite Propellants", AIAA J. 8, 370 (1970).
18. M.K. King, "Model for Steady State Combustion of Unimodal Composite Solid Propellants", AIAA Paper No. 78-216, AIAA Sixteenth Aerospace Sciences Meeting, Huntsville, AL, January 1978.
19. N. Kubota and T. Masamoto, "Flame Structures and Burning Rate Characteristics of CMDB Propellants", in Sixteenth Symposium (International) on Combustion (Combustion Institute, 1977), p. 1201.
20. R.L. Glick and J.A. Condon, "Statistical Analysis of Polydisperse Heterogeneous Propellant Combustion: Steady State", Thirteenth JANNAF Combustion Meeting, September, 1976.

3. RESEARCH AREAS IN PROPELLANT COMBUSTION AND IGNITION

Most approaches to the study of combustion and ignition phenomena begin with the hydrodynamic equations. In their most general form these equations can be written (assuming one-dimensional flow and no external forces) as[21]

$$\frac{\partial n_i}{\partial t} + \frac{\partial}{\partial x}(v n_i) + \frac{\partial}{\partial x}(n_i \bar{V}_i) - K_i = 0 \qquad (2)$$

$$\rho \frac{\partial v}{\partial t} + \rho\, v \frac{\partial v}{\partial x} + \frac{\partial P_{xx}}{\partial x} = 0 \qquad (3)$$

$$\rho \frac{\partial \hat{U}}{\partial t} + \rho\, v \frac{\partial \hat{U}}{\partial x} + \frac{\partial Q}{\partial x} + P_{xx} \frac{\partial v}{\partial x} = 0\ . \qquad (4)$$

In these equations n_i represents the density of species i at point x, $\bar{V}_i$ its diffusion velocity, and K_i its rate of formation per unit volume and time. The quantity v represents the stream velocity, ρ the density, $\hat{U}$ the internal energy per gram, Q the heat flux, and P_{xx} the appropriate element of the pressure tensor for one-dimensional considerations. It is frequently convenient to multiply Eq. (2) by m_i, the mass of the i^{th} species, and sum over i to produce

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) = 0\ , \qquad (5)$$

a continuity equation for the system as a whole. To obtain this result we have noted that the third term in the equation vanishes upon summation because of momentum conservation, whereas the fourth term vanishes because the mass is conserved in a chemical reaction.

Equations (2) - (4) simply express the conservation of mass, momentum, and energy for the system. Written as they are here, the equations are general and exact and, if one could determine all the variables in the equations, the entire combustion problem would be solved. It is evident, however, that the equations are insufficient to determine the flow variables uniquely. For instance, even if all the K_i were known with certainty (which they are not) as well as the s species present in

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[21] J.O. Hirschfelder, C.F. Curtiss, and R.B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954), Chap. 11.

the combustion process we would have too few equations to determine the 2s + 3 unknowns (s values of n_i and $\bar{V}_i$, P_{xx}, $\hat{U}$, and Q). In order to make the equations determinate, one must further assume equations of state of the form

$$n_i = n_i\,(T,P) \qquad i = 1,2\ldots s$$
$$\hat{U} = \hat{U}(T,P) \tag{6}$$

where T is the temperature and P the pressure; a form of the heat transport such as the Fourier law given by

$$Q = -\,\kappa\,\frac{dT}{dx} \tag{7}$$

where κ is the thermal conductivity; and a relation for the pressure tensor such as that given by Stokes' hypothesis, namely

$$P_{xx} = P - \frac{4}{3}\,\mu\,\frac{dv}{dx} \tag{8}$$

where μ is the viscosity. Relations (6) - (8) yield s + 3 additional equations for a total of 2s + 5, and two additional unknowns (T and P) for a total of 2s + 5, and thus the flow variables can be determined uniquely.

There are a number of difficult problems associated with this approach to the study of combustion and ignition problems. First, and undoubtedly the most serious, is that the reactions occurring during the combustion process are not known, much less the functional form of their reaction rates, K_i. Furthermore, even if the reactions and rates were known, there are probably several hundred reactions which occur in the course of the burning of a typical solid propellant. Therefore, the problem becomes extremely difficult just for computational reasons. Second, in writing Eqs. (6) - (8) one assumes the existence of at least a state of local thermal equilibrium. That is, the thermodynamic variables are assumed to be essentially constant within a distance of several mean free paths. As we shall see, such an assumption may be valid for the case of slowly burning propellants, but is almost certainly not valid for rapidly burning propellants. Not only does the absence of equilibrium invalidate use of these relations in burning-rate models, but also precludes the use of reaction rates determined under equilibrium conditions. It is well-known, for instance, that the Arrhenius reaction-rate formalism, which holds in most equilibrium situations, is not valid when reactions occur in a nonequilibrium environment[22].

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[22] K.E. Shuler, "On the Kinetics of Elementary Gas Phase Reactions at High Temperatures", in Fifth Symposium (International) on Combustion (Combustion Institute, 1955), p. 56.

Finally, even under conditions of equilibrium, the equations of state represented in Eqs. (6) are not accurately known, particularly when the substances can undergo phase changes. Furthermore, accurate values of the viscosity and thermal conductivity are not known for most substances of interest.

Most currently used models evade the problems discussed above by (1) assuming that a single, global, Arrhenius - type reaction term accounts for the chemistry in the problem, (2) that local-equilibrium assumptions are valid, and (3) that the combustion region can be divided into the zones discussed before wherein certain of the terms contained in Eqs. (2) - (4) can be neglected. Even after these assumptions have been made the solutions of the equations can be difficult and, furthermore, usually contain parameters which are not known experimentally and which must be fit to the burning-rate data. It appears that this approach with these assumptions has probably been investigated to the fullest extent possible, and that further progress is likely to come only when the chemical and physical processes occurring are more accurately represented. In the remainder of this section we shall discuss those processes needing further investigation, outline some techniques for studying them, and illustrate possible benefits from such studies.

3.1 Energy Transport.

In this subsection we will examine conditions under which one might expect conventional assumptions regarding energy transport to be invalidated by absence of local equilibrium. Primarily, the discussion will be concerned with two problems. In the first, we will investigate the applicability of the Fourier law to combustion models; in the second, we discuss the possibility of the absence of equilibrium among the molecular internal degrees of freedom below the propellant surface.

The Fourier heat law, represented in Eq. (7), is known both theoretically and experimentally to be valid only when the temperature gradients producing the heat flux are small. More quantitatively the relationship[23]

$$\frac{\ell}{T_{av}} \frac{dT}{dx} \ll 1 \qquad (9)$$

must hold where ℓ is the scattering mean free path and T_{av} the average temperature in the region under consideration. In the burning-rate problem, use of the Fourier law to represent heat conduction is most likely to fail in the subsurface zone discussed in Sec. II, for it is here that temperature gradients are steepest. Consider, for instance, a cross-sectional area of the subsurface zone (see Fig. 1) and recall

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[23] J.O. Hirschfelder *et al.*, Chap. 1.

that we study the problem from a frame which moves with the velocity of the burning front. It is assumed that the combustion process is steady in this frame. If we represent the heat released per unit volume arising from the exothermic reactions in this zone by $\dot{q}_x$, we can write the energy-conservation equation as

$$\frac{d}{dx}\left(\kappa\frac{dT}{dx}\right) - \rho\, v\, \frac{d}{dx}(C_pT) + \dot{q}_x = 0. \tag{10}$$

In obtaining this expression we have used Eq. (7). The quantity C_p represents the specific heat at constant pressure and, here, v is the velocity at which the propellant "flows" into the cross-sectional area. The equation simply states that the rates of change of heat content owing to conduction, convection, and chemical reaction must sum to zero in order that energy be conserved.

Equation (10) is difficult to solve because of the temperature dependence of κ, C_p, and $\dot{q}_x$. If we are only interested in a qualitative description of the region, however, we can assume that κ and C_p are constant. Furthermore, since the heat released is appreciable only near the surface of the burning propellant, where the temperatures are substantial, we will assume that the heat-release term can be represented by a δ- function source. Thus, we have

$$\frac{d}{dx}\left(\kappa\frac{dT}{dx}\right) - v\rho\, \frac{d}{dx}(C_pT) + \dot{q}_o\, \delta(x) = 0 \tag{11}$$

where $\dot{q}_o$ is the heat released per unit area at the plane x=0 and δ is a Dirac δ function. For convenience, we have assumed that the origin is located at the propellant surface. Equation (11) can be integrated once to obtain the discontinuity in $\frac{dT}{dx}$ at x=0, and the equation without source term can then be easily solved. When the appropriate boundary conditions have been applied, the solution of Eq. (11) can be written

$$T-T_o = \frac{\dot{q}_o}{2\alpha v\kappa}\, e^{\alpha vx} \tag{12}$$

where $\alpha = C_p\rho/\kappa$ and T_o is the ambient temperature. The temperature of the burning surface is generally more readily known (or easily measured) than the heat released by reactions and, therefore, Eq. (12) can more conveniently be written

$$T-T_o = (T_s-T_o)\, e^{\alpha vx} \tag{13}$$

where T_s is the temperature at the surface.

The width of the subsurface zone can be defined (arbitrarily) as the distance between the origin and the point at which

$$\frac{T-T_o}{T_s-T_o} = 0.01 \; . \tag{14}$$

If we denote the width by Δx, we have from Eqs. (13) and (14) the result

$$\Delta x \approx \frac{4.6}{\alpha v} \; . \tag{15}$$

It is evident that as the burning rate increases the width of the subsurface zone decreases. Consequently, for a given temperature drop across the zone, the temperature gradient must also increase with increasing burning rate. Therefore, at some value of the burning velocity, v, depending on the mean free path, ℓ, the relationship in Eq. (9) can no longer hold and the Fourier law cannot adequately represent heat transfer in the combustion problem.

It is customary to think of mean free paths in solids as being of the order of a few lattice spacings and, therefore, the relaxation times of the order of 10^{-12} seconds[24]. Suppose, for instance, ℓ=20Å, and note from Eq. (14) that the left-hand side of Eq. (9) becomes of the order of unity when

$$v \approx \frac{4.6T_{av}}{\alpha\ell \;\; \Delta T} \; . \tag{16}$$

Assuming, further, $\alpha = 10^7$ s/m^2, T_{av} = 150°C, ΔT = 300°C, we obtain from Eq. (16)

$$v \approx 10^2 \text{ m/s.} \tag{17}$$

Therefore, if the quoted values of the mean free path are accurate in the combustion problem, only for very rapidly burning propellants indeed would the Fourier law be inapplicable. Recently, however, interest has arisen in the development of such fast burning propellants especially with regard to the travelling-charge gun[25]. The above analysis indicates that the customary model calculations, undertaken for more conventional propellants, are not likely to be valid for the rapidly burning propellants. In addition, recent studies[26] of shock propagation in one-dimensional lattices have revealed the propagation of well-defined,

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[24] J.M. Ziman, Electrons and Phonons (Oxford University Press, London, 1960), Chap. 8.

[25] M.E. Levy, M. Visnov, J.F. Kowalick, M.S. Silverstein, "Hypervelocity Solid Gun Propellants" Frankford Arsenal Report No. R-1786, Philadelphia, PA, 1965.

[26] See, e.g., J.D. Powell and J.H. Batteh, "Shock Propagation in the One-Dimensional Lattice", Ballistic Research Laboratory Report No. 2009, Aberdeen Proving Ground, MD, 1977. (AD #A044791)

stable pulses known as solitons behind the shock front. The stability of these pulses tends to prevent the establishment of translational equilibrium, making the relaxation times much longer than ordinarily expected. The extent to which such effects will persist in real, three-dimensional crystals or in the combustion rather than shock-wave problem is not known. The subject, however, is appropriate for further investigation.

Probably more important than the above considerations, however, is that the discussion above really applies to only monatomic solids, and the mean free paths quoted are appropriate for translational equilibration. Solid propellants are, of course, always polyatomic and, in addition to heat conduction, relaxation of the internal modes also occurs beneath the propellant surface. As is well known, the time required for the internal degrees of freedom to relax is considerably larger than that required for translational equilibration. In fact, acoustic-resonance-absorption experiments[27] have indicated vibrational relaxation times in solids of the order of 10^{-8} seconds, some four orders of magnitude longer than the time estimated for translational equilibrium to occur. This relaxation time implies a mean free path of the order of ten microns which is approximately the length of the subsurface zone in a solid propellant having a burning rate of a few cm/sec[9]. Consequently, one can expect nonequilibrium to exist among the internal degrees of freedom in most solid propellants and the effect of the nonequilibrium upon chemical reaction rates needs to be investigated.

The study of nonlinear heat conduction (flux not proportional to temperature gradient or Fourier law not applicable) is an extremely difficult topic. Essentially the only analytic investigations undertaken to date have been via series solutions to the Boltzmann transport equation[28]. These results are only valid for the case of gases and, then, only provided the deviations from linear transport can be treated as a small perturbation. Furthermore, the general validity of the series-expansion solutions has been questioned.

In the future the most feasible approach for studying this problem as well as the relaxation process in solids is likely to be via a computer-molecular-dynamic (CMD) technique[29] (discussed in the following section). In this approach the dynamic equations of motion of the molecules in the lattice are solved numerically and, from their solution

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27. L. Liebermann, "Resonance Absorption", in Physical Acoustics, edited by W.P. Mason (Academic, New York, 1966), V. IV, p. 183.
28. J.O. Hirschfelder *et al.*, Chap. 7.
29. For discussion of technique, see B.J. Alder and T.E. Wainwright, "Studies in Molecular Dynamics. I. General Method", J. Chem. Phys. 31, 459 (1959).

one can deduce more macroscopic properties of the crystal. The technique has been used successfully in the past to simulate shock propagation in discrete monatomic lattices. By appropriately modifying the boundary conditions, it would appear possible to employ similar techniques to study the heat-conduction problem appropriate to solid-propellant combustion. The most desirable outcome of such an investigation would be to obtain an expression for the heat flux, Q, in Eq. (4) that was valid under conditions more general than are appropriate for the Fourier law.

A priori, it is difficult to tell what improvements such an undertaking would make in our theoretical understanding of solid-propellant combustion. Two possibilities, however, exist. First, a more accurate representation of the functional form of the heat-conduction term is an obvious advantage in efforts to model solid-propellant combustion, even if it remains necessary to fit certain parameters to the experimental data. Second, such a study may lead to a much more accurate characterization of the nonequilibrium environment in the subsurface zone of the burning propellant. In existing models, it is assumed that the chemical-reaction rates can be represented by an Arrhenius formalism. Such an expression is, of course, invalid unless at least local thermal equilibrium exists in the region under consideration. However, the above discussion as well as indirect experimental evidence suggests that equilibrium does not exist below the propellant surface and that the Arrhenius representation does not hold. Attempts to explain the dependence of the burning rate on initial temperature or temperature sensitivity, for instance, lead to unacceptably low values of the activation energy in the Arrhenius rate and unacceptably high values for the surface temperature[4]. This anomaly has been explained as resulting from the absence of equilibrium below the surface. An accurate characterization of the nonequilibrium environment, perhaps possible using a computer-molecular-dynamic technique, is an obvious prerequisite to obtaining a more reliable reaction-rate model.

3.2 The CMD Technique and Other Uses.

The use of CMD techniques to study highly nonlinear and nonequilibrium problems has risen rather sharply in the last few years. Most of the early efforts were directed toward using the technique to study equilibrium properties of gases, mostly to demonstrate that one could obtain the same results as expected from thermodynamics and equilibrium statistical mechanics. In more recent years, studies have been made of nonequilibrium properties of gases and solids, perhaps most extensively their response when subjected to shock compression[30,31]. This particular use of CMD techniques holds considerable promise for the future, since it represents perhaps the only feasible method for investigating highly nonlinear, nonequilibrium problems which preclude analytic approximations.

The basic idea of computer molecular dynamics is to solve numerically the equations of motion for the atoms or molecules in the system when it is subjected to the appropriate boundary or initial conditions. Once the equations have been solved, of course, all the information about the system is available in complete detail. In addition to the usual objections raised against "brute-force" techniques, one further limitation of the CMD approach is that only small systems (a few thousand particles) can be treated. Nevertheless, the method is capable of providing considerable physical understanding of the problem and, perhaps, of laying the foundation for more rigorous mathematical theories.

The possibility of using CMD to study nonlinear heat conduction and its effects upon combustion has been discussed in the last section. A number of other possible applications of this technique for illuminating unsolved problems in combustion theory should perhaps be explored as well. A few of these will now be discussed briefly.

One of the most perplexing problems in combustion studies is understanding theoretically the behavior at the surface of the burning propellant. Some substances apparently sublimate prior to the onset of chemical reactions, some melt and then vaporize, and finally some undergo substantial exothermic reactions in the solid phase. The specific mechanism is extremely important in burning-rate models, because the reaction rate is different in different cases. Phase changes and the conditions under which they occur have been under study in thermodynamics for many years. Unfortunately, for the combustion problem, however, none of these thermodynamic theories is likely to describe the phase changes which occur at the propellant surface, because the theories are based upon the assumption of thermal equilibrium while, as pointed out before, the surface is characterized by a state of extreme nonequilibrium.

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[30] D.H. Tsai, "An Atomistic Theory of Shock Compression of a Perfect Crystalline Solid", in Accurate Characterization of a High-Pressure Environment, edited by E.C. Lloyd, Natl. Bur. Stds. Spec. Publ. No. 326 (U.S. GPO, Washington, DC, 1971), p. 105.

[31] A. Paskin and G.J. Dienes, "Molecular Dynamic Simulations of Shock Waves in a Three-Dimensional Solid", J. Appl. Phys. 43, 1605 (1972).

Recently attempts[32] have been made to verify various equilibrium theories, particularly theories of melting, using the CMD approach and some success has been obtained. *A priori*, it appears possible to modify the techniques to study phase changes under the nonequilibrium conditions. Using the CMD approach, for instance, one could presumably simulate the boundary conditions which occur at the propellant surface by having the propellant "flow into" a region of constant temperature at a rate equal to the burning velocity (see Figure 3). The response of the surface to this process then will be similar to that experienced by a burning propellant and the conditions under which phase changes occur and how they compare with those occurring under equilibrium conditions can be ascertained.

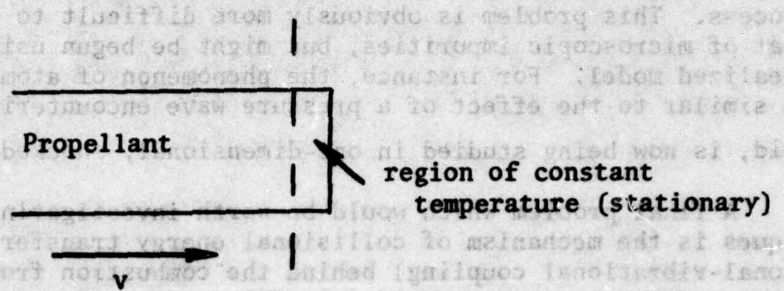

Figure 3. Model for CMD study of propellant-surface behavior.

The information which can be gained from such a study is, admittedly, somewhat limited. First, including the actual chemical reactions which occur in the solid or gas phase is obviously a long way in the future as far as CMD techniques are concerned, and at the present time one can only hope to study the physical aspects of the problem which influence phase changes. Second, a detailed knowledge of the molecular forces of the propellant will probably be necessary before any quantitative information can be obtained. Therefore, in addition to CMD studies of the type mentioned, some experimental work designed to measure the forces would be desirable. Despite these shortcomings, it would appear that such studies may be a viable initial effort in studying the effects of nonequilibrium upon phase changes. The major advantage over the thermodynamic theories is that one can actually investigate the physical processes which lead to instability in the solid, such as the formation and coalescence of dislocations and vacancies. It is likely that a thorough understanding of such effects is necessary to understand how nonequilibrium actually affects the phase change.

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[32] W.G. Hoover and M. Ross, "Statistical Theories of Melting", Contemp. Phys. 12, 339 (1974).

An additional area of study amenable to attack via CMD techniques is the effect of impurities upon the localization and relaxation of energy within the propellant. It is known, for example, that light isotopic impurities in a crystal oscillate at abnormally high frequencies and, therefore, have a higher effective temperature than the crystal as a whole. It would seem that this effect could conceivably influence the ignition properties of the solid, making ignition occur at lower temperatures than those expected from the ordinary thermal theories. In addition, impurities will certainly affect the mechanism of energy relaxation behind the combustion front and, thus, may be significant in determining the extent to which equilibrium exists beneath the surface of the burning propellant.

Along similar lines, it would also be desirable to study macroscopic voids in the solid phase and their effects upon the combustion process. This problem is obviously more difficult to investigate than that of microscopic impurities, but might be begun using a highly idealized model. For instance, the phenomenon of atomic spall, which is similar to the effect of a pressure wave encountering a macroscopic void, is now being studied in one-dimensional, shocked lattices[33].

A final problem which would be worth investigating using CMD techniques is the mechanism of collisional energy transfer (such as translational-vibrational coupling) behind the combustion front. To date, little effort has been expended in CMD studies of polyatomic systems but some studies could perhaps be undertaken on a simple scale. As was pointed out in the last section with regard to relaxation in the subsurface zone, an understanding of the specific process of energy relaxation is an absolute prerequisite to determining the factors which affect reaction rates in nonequilibrium systems and, consequently, which affect burning rates and other important parameters in the combustion problem.

The above discussion is not intended to imply that, by diligent application of CMD techniques, one will solve the combustion problem in the near future. At the present stage, the techniques can obviously be applied only to the simplest models and their relationship to real systems is rather tenuous. As we have emphasized before, however, the limit of the macroscopic theories has essentially been reached, and further understanding is likely to come only with a more detailed understanding of important microscopic processes. Progress along these lines is likely to be slow, but it is important to begin the investigation with simple models so as not to becloud the physically important mechanisms with superfluous details. As the state of the art becomes more advanced and sophisticated, the models can then be made more realistic.

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[33] A.M. Karo, private communication.

3.3 Model Accounting for Chemical Reactions.

As was pointed out earlier, perhaps the greatest fault with most theories of solid-propellant combustion is that they neglect the details of the chemical reactions occurring during the process. Indeed, it is not uncommon for the entire reaction mechanism to be represented by a single Arrhenius reaction-rate term with the activation energy fitted to the experimental data. Obviously use of such a technique illustrates considerable ignorance about the chemical reactions occurring during combustion.

In recent years some effort has been devoted to an attempt to improve the above situation and to account for the chemical reactions in some greater detail. Perhaps the earliest of these efforts was Sotter's attempt[34] to describe the chemical kinetics of reactions beginning at the inner edge of the preparation zone (see Fig. 1) and occurring throughout the flame zone in a double-base propellant. Sotter's calculation was, at least from the point of view of modeling, a significant advance in the state of the art. Although the specific calculation contained some assumptions that could perhaps not be completely justified, the physical significance of the assumptions and what was needed to improve upon them were clear. Because of its importance, we will briefly describe the calculation and indicate some specific improvements that could perhaps be made. Most of the uncertainty in the model lies in the experimental values of the reaction rates used and their applicability to the problem at hand. In the following section we will then indicate some of the problems associated with obtaining reliable reaction rates and some of the possible methods of attack for this difficult problem.

At the time of Sotter's calculation (and now, too, for that matter) the chemistry which occurred beneath the propellant surface and in the fizz zone was largely unknown. Experimental measurements had been made of species concentrations in regions beyond the fizz zone, however, and it was in these regions that Sotter sought to explain the combustion process. He chose cordite for his analysis because it is probably the simplest of all double-base propellants, consisting primarily of nitrocellulose and nitroglycerin. It was assumed that a series of twenty elementary reactions occurred among the twelve species experimentally observed in the regions considered, and equations similar to Eqs. (2) - (8) were written down. The total number of equations to be solved was seventeen and a computer code was written to perform the numerical solution. The initial conditions for the various quantities were taken from the experimental data of Heller and Gordon[35]. The principal simpli-

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[34] J.G. Sotter, "Chemical Kinetics of the Cordite Explosion Zone", in Tenth Symposium (International) on Combustion (Combustion Institute, 1965), p. 1405.

[35] C.A. Heller and A.S. Gordon, "Structure of the Gas Phase Combustion Region of a Solid Double Base Propellant", J. Phys. Chem. 59, 773 (1955).

fying assumptions in the model were that (1) conduction and radiation of heat and diffusion of species could be neglected, (2) the flow was steady, laminar, one-dimensional and nonviscous, and (3) the internal degrees of freedom were in thermal equilibrium at the translational temperature. These assumptions, as well as the fact that the chemistry assumed to occur in the flame region may not be completely accurate, no doubt affect the validity of the result quantitatively, but in no sense detract from the value of the calculation. Furthermore, they were probably a minor source of error compared with the uncertainty in the experimental rate constants used in the calculation.

The specific results of the Sotter calculation were somewhat less important than was the demonstration that at least some details of the chemical kinetics could be included in the model. The results were, however, in reasonable agreement with the experimental data. That is, it was observed that a long preparation zone across which few reactions occurred was situated next to the fizz zone and followed by a so-called "explosion" zone in which the temperature rapidly rose. The calculated length of the preparation zone was in reasonably close agreement with experimental measurements. The results also indicated that three of the twenty assumed reactions were of particular importance and, thus, should be isolated for further study.

The Sotter calculation first gave a reasonable estimate of the chemical processes which occurred during combustion in the two zones considered. The model could, of course, be applied to the fizz zone or, with greater difficulty, to reactions in the solid phase. The absence of definitive experimental data regarding reactions in either of these zones, however, precludes investigation at the present time. Nevertheless, the problem represents a challenging and worthwhile objective for the future.

3.4 Reaction Rates.

As we indicated in the previous section, the likeliest source of error in the model suggested by Sotter is the difficulty in accurately representing the chemistry occurring and in obtaining reliable reaction rates to use in the conservation equations. The entire study of reaction rates is a difficult field, and there are really three basic problems associated with it insofar as combustion is concerned.

First, there exist many theories for calculating reaction rates, ranging from the largely empirical to the highly sophisticated, but the difficulties associated with making calculations with the more reasonable theories are presently insurmountable. Even if one assumes, for instance, that the reaction rate can be represented by an Arrhenius term, viz.,

$$k = A\, e^{-E/RT}, \tag{18}$$

theoretically determining A, the pre-exponential factor, and E, the activation energy, poses a considerable problem. To do so one must know the "potential-energy surfaces" which give the potential energy of the reactants as a function of their geometric configuration and which characterize the details of the collision process. Such calculations have been carried out only for the simplest reactions.

Second, if one attempts instead to use experimentally determined rates in combustion modeling, he finds that much uncertainty exists in the quoted values. As Sotter suggested, this uncertainty was the major source of error in his calculations. It is clear, therefore, that more accurate experimental determination of the rate constants is as desirable as better theoretical techniques.

Finally, and perhaps most important, it should be pointed out that reaction rates determined theoretically or experimentally, under some ideal set of conditions, may be totally inapplicable when used in the combustion problem. For example, the Arrhenius reaction rate of Eq. (18) is fairly well obeyed for most reactions provided the system is not too far from thermal equilibrium. One cannot expect, however, that such a rate can describe reactions under highly nonequilibrium conditions such as in the presence of steep temperature gradients referred to earlier or if the reactions themselves are sufficiently rapid to disturb the system from equilibrium. Even if the functional form of Eq. (8) is still obeyed, the values of the activation energy and temperature needed to obtain agreement with experiment may bear little relationship to their actual values. Under these circumstances, one must be especially careful to be certain that the conditions under which the rates are derived or measured apply to the problem at hand.

As pointed out, a number of theories exist for calculating reaction rates under equilibrium conditions. It is perhaps fair to say that the main limitation of all the theories is that the potential-energy surfaces are very difficult to calculate. In principle, the formalism for performing the calculations exists but, in practice, many-electron, quantum-mechanical calculations still represent *terra incognita*. There are, however, a number of empirical and semiempirical methods that have been reasonably successful in approximating the surfaces, and much effort is currently being expended in improving the approximation techniques. Until the state of the art of performing rigorous quantum-mechanical calculations has been significantly advanced, however, it is unlikely that much can be done to improve the accuracy of these calculations.

On the other hand, it does appear possible that progress could reasonably be expected if one pursued either of the second two problems mentioned at the beginning of this section. Possible experimental efforts to measure reaction rates and conceivable benefits gained from them will be discussed in the following section. In the remainder of this section we will discuss those conditions which may invalidate the use of reaction rates determined under equilibrium conditions or, more generally, deviations from the Arrhenius formalism. Some suggestions for theoretically investigating the rates under such conditions will then be discussed.

One of the commonest conditions under which the equilibrium assumption fails and deviations from the Arrhenius-type reaction rate occur is at high temperatures when the reactions are very rapid[22]. Under such conditions the rate of chemical reactions becomes faster than the rate at which collisions can restore equilibrium to the molecules in the system or among the various degrees of freedom within a given molecule. Consequently, the reaction process itself introduces a significant perturbation to the thermal equilibrium of the system and the Arrhenius formula, whose validity depends on equilibrium, fails. Intuitively, one would expect that sizable deviations might occur whenever the temperature was sufficiently high that RT became of the same order of magnitude as the activation energy. Some theoretical considerations[36] have revealed that the condition is more accurately given by

$$\frac{E}{RT} < 10. \tag{19}$$

Experimental evidence of nonequilibrium energy distributions arising when Eq. (19) holds has been discussed by Shuler[22] in a rather old but still informative paper.

It is of interest to look at some of the reactions assumed by Sotter in his calculation for which he used (perhaps out of necessity) equilibrium reaction rates. In Table I are listed several of the reactions along with their activation energies[37] and the ratio, E/RT. The temperature listed is approximate and activation energies are a rough average of those listed for a particular reaction. From the table it can be seen that for the first three reactions Eq. (19) holds, and one can expect that the rates used by Sotter, derived under equilibrium conditions, will not be valid. In particular, the reaction

$$H_2O + H \rightarrow H_2 + OH \tag{20}$$

was found by Sotter to be one of the three most important which occurred in the explosion zone. From the results in the table, however, use of equilibrium reaction rates to represent the reaction is almost certain to fail and more reliable rate constants are much needed.

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[36] E.W. Montroll and K.E. Shuler, "The Application of the Theory of Stochastic Processes to Chemical Kinetics", in Advances in Chemical Physics, edited by I. Prigogine (Interscience, New York 1958), p. 361.

[37] Data taken from Gilbert S. Bahn, Reaction Rate Compilation for the H-O-N System (Gordon and Breach, New York, 1967).

TABLE I. EXAMPLES OF REACTIONS IN SOTTER CALCULATION.

Reaction	$E(\text{cal}/\text{mole}\cdot\text{gram})$	T(°K)	E/RT
$O+H_2 \rightarrow H+OH$	8000	2500	1.61
$H_2O+H \rightarrow H_2+OH$	20,000	2500	4.0
$H+O_2 \rightarrow O+OH$	16,000	2500	3.2
$H+H+NO \rightarrow H_2+NO$	52,000	2500	10.4
$O+H_2O \rightarrow H+HO_2$	55,000	2500	11.0

Theoretical attempts to account for the effects of nonequilibrium upon reaction rates in fast reactions have been summarized by Shuler[22] and by Laidler[38]. Theoretical treatments are, of course, made doubly difficult because, not only are the potential surfaces unknown, but deviations from an equilibrium or Maxwellian distribution must also be accounted for. Consequently, most of the theoretical attempts have been rather general and have stressed the nonequilibrium aspects of the problem. In particular, they do not consider specific potential-energy surfaces and, therefore, are not applied to specific reactions. There is, of course, always the possibility that such details can be included in the theories in the future but, realistically, the ability to do so looks singularly unpromising.

In addition to the cases mentioned previously, other examples of reactions occurring under nonequilibrium conditions have been observed. It has been found, for instance, that some molecules undergo unimolecular decomposition before the vibrational energy of the molecule has been randomly distributed among its internal modes[39,40]. As a result, the chemical-reaction process is complicated by vibrational relaxation which proceeds in parallel with it, and deviations from the Arrhenius rate occur. The effect is especially pronounced at high pressures. Some

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[38] K.J. Laidler, Theories of Chemical Reaction Rates (McGraw-Hill, New York, 1969), Chap. 8.

[39] J.D. Rynbrandt and B.S. Rabinovitch, "Intermolecular Energy Relaxation.Nonrandom Decomposition of Hexafluorobicyclopropyl", J. Phys. Chem. 75, 2164 (1971).

[40] B.S. Rabinovitch, J.F. Meagher, K.J. Chao, and J.R. Barker, "Failure of Intramolecular Energy Relaxation in Unimolecular Reaction Systems", J. Chem. Phys. 60, 2932 (1974).

theoretical consideration[41] has been given to the mechanism by which the process occurs and under what experimental conditions, but the phenomenon is still far from understood.

At least for the present time, the most reasonable approach to the study of nonequilibrium reaction-rate phenomena appears to be molecular dynamics[42]. This technique is essentially the same as that discussed in Sec. 3.2. Specifically the reaction is described by numerically solving the classical equations of motion of the reactants as they undergo a collision and (sometimes) participate in a reaction. Quantum effects can be considered only insofar as they affect the initial distribution function of the system. The potential-energy surfaces appropriate to the reaction must be provided since the differential equations of motion depend, of course, upon the potential interaction. In order to have any statistically meaningful results each equation (classical trajectory) must be solved a large number of times corresponding to various initial conditions. After perhaps a thousand reactive collisions, the details of the reaction process such as rate constants and cross sections can be inferred.

The molecular-dynamic approach of studying chemical reactions is a laborious and time-consuming technique. An immense amount of computer time is required to calculate a single rate constant and, to date, the technique has been used primarily to demonstrate simply that calculations were feasible. It does appear reasonable, however, that in the future the method could be used to study reactions under nonequilibrium conditions. In that case, the CMD methods discussed earlier become an extremely useful adjunct to the technique, because they can provide an accurate initial nonequilibrium distribution function required before the calculations can begin.

3.5 Diagnostic Techniques.

So far, we have discussed various problems that might arise if investigators rely upon macroscopic assumptions used in combustion studies, and have suggested some theoretical techniques for resolving these problems. It is obviously desirable to accompany theoretical treatments with as complete an experimental program as possible. In this final section we will briefly discuss some relatively new diagnostic techniques, indicate the types of measurements which they can now make or soon may be used to make, and suggest how they can further our knowledge of combustion. The discussion will be restricted for the most part to optical diagnostic techniques. The techniques and their applications to combustion

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[41] I. Oref, "Nonrandomization of Energy in Unimolecular Reaction. The Effects of High Pressure on the Apparent Rate Constant", J. Chem. Phys. 63, 3168 (1975); "Nonrandomization of Energy at High Pressures in Photochemical Systems", J. Chem. Phys. 64, 2756 (1976).

[42] For discussion of technique, see Laidler, Chap. 7.

problems have been discussed in greater detail in the proceedings[43] of a workshop on combustion measurements and, in a more tutorial manner, in a report[44] by Eckbreth, Bonczyk, and Verdieck.

Probably the simplest of the optical diagnostic techniques is the process of laser Doppler velocimetry (LDV). Although the technique has limited applications, it does provide a reliable and extremely accurate method of measuring particle velocity. The procedure relies upon the elementary principle that radiation scattered from a moving object is shifted in frequency by an amount depending upon the object's velocity. Thus, by irradiating a sample of gas with coherent light, collecting the scattered light, and measuring the frequency shift, the observer can ascertain the flow velocity of the sample. The advantages of LDV over more conventional techniques are that it does not perturb the system under study, that it is extremely accurate since only frequency shifts need be measured, and that rather good spatial resolution can be obtained. (Measurements[45] have been made which claim a spatial resolution of approximately 1 mm^3.) Probably the greatest source of inaccuracy in the procedure results from fluctuations in refractive index along the optical path of the incident and scattered beams. Particularly in combustion studies, it would appear that this problem could be significant because of sizable temperature and density gradients.

In addition to measuring flow velocities in general, a promising application of LDV lies in experimental studies of turbulence. Theoretical models describing this important phenomenon depend upon fluctuations in the velocity of small segments of the fluid about the mean flow velocity, as well as certain correlations in these fluctuations[46]. The theory of turbulence is probably the most difficult topic in fluid mechanics and the models used to describe it are not totally convincing. Some experimental verification as well as ideas for better models are, therefore, highly desirable. Efforts[47] have already been made in measuring turbulent velocities, but the correlations remain a problem for future study.

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[43] R. Goulard, editor, Combustion Measurements (Academic, New York, 1976).

[44] A.C. Eckbreth, P.A. Bonczyk, and J.F. Verdieck, "Review of Laser Raman and Fluorescence Techniques for Practical Combustion Diagnostics", United Technologies Research Center Report No. R77-952 665-6, Hartford, CT, 1977.

[45] C.P. Wang, "Velocity", in Combustion Measurements, edited by R. Goulard (Academic, New York, 1976) p. 392.

[46] See, for instance, R.A. Strehlow, Fundamentals of Combustion (International Textbook Company, Scranton, Pennsylvania, 1968), Chap. 8.

[47] F.K. Owen, "Laser Velocimeter Measurements of a Combined Turbulent Diffusion Flame Burner", in Combustion Measurements, edited by R. Goulard (Academic, New York, 1976), p. 91.

A technique rather more versatile than LDV is Raman spectroscopy (RS) since its use can, at least in principle, allow one to measure temperature and concentrations of a given species. The technique is based upon the inelastic scattering of light from the species under consideration with the observed frequency shift being dependent upon the internal energy-level structure of the molecule. Consequently, if the internal structure is known as well as appropriate cross sections, the population of various levels can be inferred from the intensities of the spectral lines. Temperature (if the system is in equilibrium) and density are then related to these data in a fundamental way.

There are two primary advantages to using RS. First, the method is specific; that is, individual species and their energy-level populations can be identified by the spectral lines. Second, the technique can be used to study systems which deviate substantially from thermal equilibrium. Therefore, it offers, for instance, some promise of yielding experimental information about nonequilibrium reaction rates discussed in the last section. In addition, the method has been found to be highly accurate (within about 5%) for measurements of $T_{vibrational}$ and $T_{rotational}$[48] and of density and to have a spatial resolution of about 1 mm^3[49]. The major disadvantages of the technique are that the scattering cross sections are small and, thus, the intensities of the spectral lines weak, and that information concerning the energy levels of the species must be available. As pointed out previously, the major application of RS consists of measuring temperature and species concentrations in burning gases. Efforts[43] to do so are well underway.

Closely related to RS is a diagnostic technique referred to as laser excited fluorescence (LEF). The procedure is similar to RS except that one uses a laser which emits radiation at a frequency close to an absorption line in the molecule. At these particular frequencies the scattering cross sections are considerably larger than those for RS and, consequently, much more intense spectral lines can be observed. For this reason, the technique is especially useful in measuring the concentration of minor species in fluid flow since their spectral lines are often unobservable in RS. For the increased intensity, however, a considerable price must be paid. First, one must obviously have available a laser which lases at the desired frequency. This severely limiting problem has been ameliorated somewhat in the last few years with the development of tunable lasers, but more progress is obviously desirable. A second disadvantage results whenever the fluorescence

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[48] S. Lederman, "Temperature", in Combustion Measurements, edited by R. Goulard (Academic, New York, 1976), p. 402.

[49] A. Fontijn, "Concentrations", in Combustion Measurements, edited by R. Goulard (Academic, New York, 1976), p. 397.

decay time is longer than the time required for collisional relaxation of the molecule. Obviously, under these conditions quenching occurs and the intensity of the observed lines is not representative of the population of the internal states. Unfortunately, this effect is most likely to occur at high pressures which are of interest in most combustion problems. Other than the above differences, however, LEF is similar to RS and amenable to use for the same types of measurements. Furthermore, the spatial resolution and accuracy of the two methods is about the same. Used together in a complementary fashion, the two procedures offer considerable promise of yielding complete temperature and density profiles in burning systems. Accomplishment of such an objective, however, lies in the future and is contingent upon further development of tunable lasers and knowledge of the fundamental properties of the gases under investigation.

Other diagnostic techniques are frequently used in combustion study and might be mentioned briefly. Rayleigh scattering, for instance, which is elastically scattered radiation, is often used in density measurements. The cross sections for Rayleigh scattering are larger than those for RS and, thus, the scattered light is more easily observed. The severe disadvantage of Rayleigh scattering in combustion work is the lack of specificity (inability to discern individual species). This disadvantage can be overcome with so-called Coherent Anti-Stokes Raman Spectroscopy, a nonlinear optical process, which has the property of specificity and yet produces more intense spectral lines than RS. The technique is still being developed, but is a promising candidate for future study. Other techniques used in combustion diagnosis include holography, material probes, and various other laser-related scattering processes. These techniques, however, are either less well developed or less desirable for use in combustion than those mentioned above.

It would appear that optical diagnostic techniques, when further refined, can yield much information about combustion in general and perhaps lead to more appropriate models. For example, only a slight improvement in RS resolving power should permit at least some experimental analysis of the fizz zone. Lack of information about reactions occurring there has been a long-standing problem in solid-propellant combustion, and resolution of the problem could lead to an analysis similar to that undertaken by Sotter for the cordite explosion zone. In addition to identifying species present during the burning process, some of the techniques can also be used to measure relaxation times and reaction rates, even though the reactions may occur under conditions of nonequilibrium . An experimental study designed to do so would be an important complement to the theoretical work suggested in the preceding section.

4. SUMMARY AND CONCLUSIONS

We have given a brief, qualitative review of some of the basic assumptions employed in the macroscopic treatment of combustion problems. The conditions under which the assumptions were expected to no longer hold were enumerated, and some techniques for further study of the physical and chemical processes important in combustion were described. It was emphasized that the combustion problem involved many complicated, poorly understood, long-standing problems in basic chemistry and physics, and that further understanding of combustion was possible only when these problems had been resolved and the results incorporated into new or current models.

The principal conclusions reached were as follows:

1. Energy transport beneath the surface of the burning propellant can occur under highly nonequilibrium conditions particularly in rapidly burning propellants. An effort should be made, using CMD techniques, to obtain a more reliable expression to represent the heat transport term under these conditions.

2. Phase transitions at the surface of the propellant occur under conditions of extreme nonequilibrium and the usual thermodynamic approaches to the problem do not apply. By appropriately selecting the boundary conditions, it appears possible to use CMD techniques to study the effects of nonequilibrium and an effort should be made to do so.

3. CMD techniques should also be extended to study collisional energy transfer in regions of non-equilibrium and to study the effects of impurities upon relaxation and upon initiating reactions. Similar studies have been conducted or are underway with regard to the shock-wave problem.

4. Future modeling attempts should strive to include the important chemical reactions in the burning process as, for instance, Sotter has done in his description of the cordite explosion zone. Such a calculation applied to the fizz zone would be particularly useful.

5. Equilibrium, Arrhenius reaction rates will be valid only, at best, when the activation energy is much larger than the thermal energy. A number of reactions important in combustion do

not satisfy this condition and an effort should be made to study theoretically the effects of nonequilibrium upon the reaction rates. The trajectory calculations of molecular dynamics offer the most feasible approach to this problem.

6. Recently developed optical diagnostic techniques offer considerable promise in being able to discern the concentration of species at various locations in the burning system and for measuring reaction rates, especially under nonequilibrium conditions. Emphasis should be placed upon continuing development and refinement of these techniques. Especially worthwhile advances would be slightly better spatial resolution, more diverse tunable lasers, and, of course, more information concerning the internal structure of the molecules under study.

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