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Final Report

THEORY OF STEADY AND UNSTEADY COMBUSTION OF SOLIDS

Period of Contract Research

October 1, 1958 to February 28, 1963

by

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Principal Investigator

1. INTRODUCTION

This final technical report will summarize the research done under Contract AF 49(638)-412, "Theory of Steady and Unsteady Combustion of Solids," from October 1958 to February 1963. The general purpose of this study has been the development of analyses of mathematical models for the burning of solid propellants. The principal aim of such analyses has been the investigation of the effects of various fundamental parameters upon the magnitude of the steady burning rate of propellants and upon the conditions for stable steady combustion.

The approach has consistently been through theoretical formulations derived from the basic conservation equations for mass, momentum and energy transport in the mechanics of continua, coupled with auxiliary relations defining the rates of chemical reactions, of diffusive transport and so forth. This approach had been well established in the scientific literature before the inception of this research. It may be described by the term "phenomenological combustion theory." The term "aerothermochemistry" is also used. A basic reference which has been used for the background of this field, is the book Chemistry Problems in Jet Propulsion, by S. S. Penner.

In this introductory section, some important but general features of our work will be summarized. Discussion of specific details will be made in the following sections. In all of the theoretical work which has been done, it has been necessary to strike a balance in the setting up of mathematical models for the analysis. It is realized quite rapidly by anyone investigating applied problems in phenomenological combustion theory that a priori information for a complete analytic description is lacking even in the simplest cases. By this we mean not merely that certain numerical data is lacking on magnitudes of physical constants. This is part of the difficulty in applications, of course. More fundamentally, the functional forms of the kinetic functions describing rates of gas-phase or condensed phase chemical reactions must be assumed. A basic assumption in phenomenological combustion theory is the description of rates of chemical reactions in a flowing gas by use of the law of mass action, which assumes chemical equilibrium at the local thermodynamic state in the gas. The transport relations are also assumed to be independent of the chemical reactions. Moreover, the details of chemical kinetics for the gas-phase combustion reactions are unknown for any real propellant system.

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The gas-phase reactions can at best then be treated in the analysis as single-step reactions, e.g., reactants \rightarrow products.

Essential features of the combustion process would be lost, however, if even the single-step reaction were not described by the mass-action principle. The introduction of the mass-action law into the conservation equations to determine the rate of generation of product gases by chemical reaction brings into these equations a characteristic, non-linear dependence upon temperature and upon reactant concentration. It also brings in at least two undetermined parameters, the activation energy and the preexponential factor from the reaction rate coefficient. Values for these parameters in a specific problem must be obtained indirectly by comparing the numerical values computed from the analysis with experimental burning-rate data.

The analyses which have been done all assume then a one-step, gaseous reaction; in some cases this reaction has also been considered to be reversible. From the work which we and others have done, the one-step chemical reaction model appears to be an adequate description for predicting, with engineering accuracy, the behavior of steady burning rates. What is actually being prescribed by the one-step assumption is that the heat released by the chemical reaction be a unique function of the temperature and of the concentration of a single reactant species, for it is the spatial distribution of this heat release which is ultimately one of the major influences of the magnitude of the steady burning rate.

The approximation of the molecular diffusion process by Fick's law for mass diffusion, and the neglect of thermal and pressure diffusion, is probably at least consistent with the one-step chemical reaction assumption. Another assumption which has been used in all of our work, and which is vital to the extreme simplicity to the results obtained, is that the Lewis number is unity. This assumption is valid for an ideal monatomic gas, and it is probably no worse an approximation than those already used. Again, the principal advantages for the use of Lewis number unity assumptions were known at the beginning of this contract work.

2. RESEARCH ACCOMPLISHED

The principal extension of phenomenological combustion theory which has been achieved by our work is to the combustion of solids, both homogeneous and heterogeneous solids. As can be seen from Penner's book, the basic equations of phenomenological combustion theory had previously been applied to systems in which the unburned reactant was already in the gaseous state. A system of relations in phenomenological combustion theory which described the progress of a deflagration wave front through a quiescent combustible gas was known as laminar flame theory. At the time when the present research began, the one-dimensional laminar flame equations had already been investigated by many authors. Approximate analytic solutions and solutions by numerical integration for particular parametric values were known. Apparently, however, little attention had been paid to the problem of a laminar flame in a reactant gas which had been formed by decomposition of a condensed phase. The overall steady rate of such a system (i.e., the rate of flow of mass per unit area) would be influenced both by the laminar flame speed in the gas and by the linear rate of decomposition of the condensed phase. For steady burning, both the flame speed and the condensed phase decomposition rate are constrained to give the same overall rate of mass flow, and this overall rate, expressed as a linear velocity, is the burning rate.

Much of the mathematical research which has been already completed under this contract has been involved with the one-dimensional laminar flame problem for a monopropellant (5), (11).^{*} In these papers there is given for the first time, so far as the authors can determine, a mathematically rigorous proof of the existence and uniqueness of solutions to a general formulation of the laminar flame monopropellant problem. The basic mathematical function which is used in calculations of the burning rate-pressure relation is called the laminar flame eigenvalue. This eigenvalue, which, in our formulation, is a positive number, is determined as part of the mathematical solution. In one part of our work, we have given a procedure to compute rigorous upper and lower bounds for the laminar flame eigenvalue. In certain applications (e.g. (6)), it has been shown that these bounds are often so close together that either bound is an adequate means for calculations of burning rates. For refined calculations, there has also been given, (5), an algorithm for calculating a strictly monotone, convergent sequence of successive approximations which allows the laminar flame eigenvalue, as well as the solutions for temperature and mass fractions, to be obtained numerically to within any prescribed degree of accuracy. These calculations involve only the evaluation of definite, nonsingular integrals.

The monopropellant theory just mentioned contains, as a special case, the laminar flame theory which is discussed in Penner's book. In particular, the bounds on the laminar flame eigenvalue exhibit singular behavior when the heat transferred back to the "cold boundary", or "flame holder", tends toward zero. The precise mathematical nature of this difficulty had never been explained, although its physical significance was apparently well understood by the leading theoreticians. In (11), a rigorous investigation of this problem has been made. It is shown in (11) that when a solution exists to the mathematical problem for strictly zero heat transfer, the solution will be non-unique. That is, there will be for this problem a continuum of eigenvalues, and the largest eigenvalue in this continuum is the limit, as the heat transfer tends to zero, of the eigenvalue which is uniquely determined for each positive value of heat transfer.

The mathematical nature of the monopropellant problem being therefore well understood, and relatively simple methods having been discovered to compute the solutions for this problem (relative simplicity being important because of the laborious nature of the calculations needed to determine empirical values for the unknown gas-phase, chemical reaction-rate parameters), it was felt desirable to test the predictions of this theory against data from a suitable experiment. Data from experiments on the burning of strands of pure pressed ammonium perchlorate became available at the time the mathematical investigation was undertaken. These experiments show that a steady burning could not be obtained if the pressure was below about 20 atmospheres. Spalding had shown in 1957 ((6), Ref. 8) that the introduction of non-adiabatic effects into laminar flame theory could result in the production of low-pressure deflagration limits. In order to obtain a complete agreement with the experiments in ammonium perchlorate deflagration, and to assure ourselves and others that this mathematical model was sufficient to describe the

* Numbers in () refer to corresponding items in the reference list at the end of this report.

burning of ammonium perchlorate under a variety of conditions that it would encounter in a composite solid propellant, the laminar flame monopropellant theory was investigated for non-adiabatic conditions. Experimental as well as theoretical calculations indicated that, for the ammonium perchlorate experiments, the principal mode of energy loss was radiant. The energy emission from the equilibrated reaction products was examined in detail (3), and its effect on the combustion was compared (2) with the effect of radiant energy emission from the hot solid surface. The latter effect was found to be very much more important. A mathematical proof of the existence of deflagration limits for the monopropellant problem assuming a surface rate law, and assuming non-adiabatic effects arising from the solid phase only, was also given in (6).

Agreement of the theory in (5) with the ammonium perchlorate experiments (6) was satisfactory in some respects but not in others. There was poor quantitative agreement with the magnitude of the low pressure deflagration limit and with the burning rate in experiments in which steady deflagration was maintained at low pressures by the addition of radiant energy from an external source. In particular, the predicted surface temperature at one atmosphere seemed too high. Now, as has been mentioned above, the burning rate for a monopropellant is determined by an equality between the laminar flame speed and the rate of decomposition of the condensed phase. The theoretical basis for determining the condensed phase decomposition was considerably weaker than that for determining the laminar flame speed. We will refer to the relations determining the rate of condensed-phase decomposition as the "surface condition," making the assumption that the decomposition occurs in so narrow a zone that it may be regarded for analytical purposes as a mathematical plane at a definite surface temperature. The surface condition used in (6) was a surface pyrolysis law, using data approximately as found from hot-plate pyrolysis experiments which had been reported in the literature by other experimenters. Our concern was on the applicability of this data to combustion processes. The pyrolysis law states that the burning rate is a uniquely defined function of surface temperature, and that it does not depend explicitly upon total pressure, reactant partial pressure, or rate of heat transfer to the surface. The surface condition is then said to be rate-controlled. If, on the other hand, there were also possible, under certain conditions, an equilibrium at the interface between the condensed phase and gaseous phase of the reactant, and if this was the case as opposed to the rate process, the effect on burning rate would be considerable. Investigations related to this problem were included in the analysis of an idealized hot plate linear pyrolysis experiment (7), and it was shown that the results of hot-plate pyrolysis experiments could not be unequivocally interpreted for application to combustion processes.

The interest that has been shown in this contract research towards application to ammonium perchlorate did not arise only from a desire to test the applicability of the assumptions made in the laminar flame monopropellant model. A central purpose of the contract research was to describe the burning of composite propellants. A close functional relationship between the monopropellant behavior of pure ammonium perchlorate and the burning rate-pressure for composite propellants using ammonium perchlorate as oxidizer have been demonstrated experimentally by a number of investigators. It seemed then essential that, in order to obtain a useful description of composite propellant burning, this monopropellant behavior of the oxidizer be included in a mathematical model. Conventional composite solid

propellants are composed of fine particles of ammonium perchlorate together with metallic additions all held together in a plastic or rubbery binder which serves as fuel. A rigorous model for this arrangement of fuel and oxidizer would encounter mathematical complexity out of proportion to the other uncertainties which already exist in the theory. In the research done under this contract on composite propellant burning, the model of the composite propellant which has been assumed is an idealized "sandwich" composite, composed of alternating slabs of fuel and oxidizer, the slab thickness being of the same order (20-200 microns) as the diameters of the oxidizer particles in actual propellants. This array is assumed to burn at a steady rate in a two-dimensional picture in which gaseous jets of decomposed solid fuel and oxidizer are issued side by side from the regressing surface, mixing by molecular diffusion in the gas phase, and supporting the steady burning by heat released in the chemical reaction between them. A rather simple solution to this problem was obtained in (4) under the principal additional assumption that the problem was diffusion-controlled. To obtain numerical values of burning rates from this solution, the surface condition for fuel and oxidizer was assumed to be described by pyrolysis laws. The sandwich burner theory was extended in (9) to account for initial non-stoichiometric compositions of the condensed phase. Although the diffusion-control assumption made into the analysis precluded a discussion of the pressure-burning rate relation, it was possible, however, to compare the predicted relation between burning rate and stoichiometry with the results of experiments done at high pressures. These results are described in (9), and the agreement was reasonable.

Since there was success in formulating and solving a complete mathematical theory for the steady burning of the monopropellant, attention was devoted during the last year of the contract research to unsteady problems in the same geometry. Examples of the unsteady problems investigated are: 1., the behavior of burning under harmonic variation of the total pressure at infinity; and, 2, the time history during ignition of a monopropellant from a radiant source. There was completed and published only one investigation on the first problem (10); this was a relatively straight forward analysis of the extension of our steady model.

We have also attempted to look at geometries for steady monopropellant burning other than the one-dimensional linear. There is a partially completed investigation of the mathematical properties in the spherical geometry. While some of our results are new, the theory is not nearly so neat and complete as was the case for the linear geometry, and some questions of existence and uniqueness of solutions still remain unanswered at the conclusion of the period of contract research.

Other research in which work has been done without reaching the point of a publishable paper is noted briefly. As concerns the steady linear monopropellant model, we have investigated the relaxation of the Lewis number unity assumption, and also the analysis of deflagration limits in the case of important energy loss from the gas phase. Neither of these investigations have reached a significant and publishable conclusion. There are on hand also improvements in the sandwich model which account for finite gas-phase reaction rates. Since the prediction of this model as applied to ammonium perchlorate depends strongly on the surface condition used for ammonium perchlorate, and since the surface condition is still being investigated, as is discussed in the following section, further calculations with the sandwich, beyond those given in (9), were not carried out during the period of contract research.

3. CONCLUDING OBSERVATIONS

Progress in the application of phenomenological combustion theory to the construction of useful theories of solid propellant burning has been reviewed in Chapter 4 of the recent book Chemical Rocket Propulsion and Combustion Research by S. S. Penner (Gordon and Breach, London, 1962). The tone of cautious optimism expressed in this book is shared by the present writer. Optimism is deserved because, through continued development of mathematical and physical models, and with fundamental experimental data becoming available, this theory does show promise of being useful. The overtone of caution is also necessary, for it would appear that a good deal of hard work remains in order to demonstrate that a theory which would predict the pressure-burning rate curve, beyond merely curve-fitting through adjustable parameters, has been established even for one propellant composition. The necessary information appears to be coming to hand for ammonium perchlorate.

We believe that a reasonably complete theory for the burning of ammonium perchlorate as a monopropellant can be developed. We are now in process of completing calculations for a paper which will also discuss the theoretical basis for applying the Knudsen-Langmuir equation as a general surface condition for the burning of a monopropellant. Experimental data on the equilibrium vapor pressure of ammonium perchlorate was recently reported by S. Inami, W. A. Rosser and H. Wise, in a preliminary report from the Stanford Research Institute. This, together with surface temperature data recently reported by J. Fowling and W. A. W. Smith (E.R.D.E. 10/K/62), provide an important part of the needed data for application of this general surface condition to ammonium perchlorate deflagration.

If the essential mechanisms controlling the deflagration of ammonium perchlorate can be identified and combined into a workable theory, then, as we see it, a number of benefits will follow. Firstly, there will be increased confidence that, in spite of the drastic simplifications made, phenomenological combustion theory is useful. Secondly, there will be a basis for advancing work on the mathematical description of the burning of composite solid propellants using ammonium perchlorate as oxidizer. A useful tool for investigating this problem, both theoretically and experimentally, is the "sandwich" composite solid propellant which we have proposed. Attempts to construct an experimental sandwich propellant were described by C. C. Ciepluch and L. A. Povinelli of the NASA Lewis Research Center, at the Fifth AFOSR Contractor's Meeting on Combustion of Solid Propellants, March 6, 1963. The slab thicknesses in these experiments were too large to achieve steady deflagration through diffusion, but the direction of the experiments is encouraging. Thirdly, there are new, high-energy oxidizers which are now in the process of costly and time-consuming development. It appears quite reasonable to expect that a guide to a fruitful method of investigating the behavior of these new compounds would be found if the procedures used successfully in the investigation of ammonium perchlorate were followed.

4. ACKNOWLEDGEMENTS.

This seems to be an appropriate place to express our appreciation that we received something more than financial support from the Air Force Office of Scientific Research for this contract work. The yearly AFOSR Contractor's Meeting on Combustion of Solid Propellants have provided us with a unique and invaluable opportunity to exchange information and ideas with other contractors on the basis of personal contact. We have also received sound advice and encouragement from the technical supervision in the Propulsion Division of the Air Force Office of Scientific Research. In this regard, I conclude this Final Report with a particular expression of my thanks to Dr. Joseph F. Maxi, Dr. Milton M. Slawsky, and Col. Paul G. Atkinson, USAF, each of whom have, at various periods, been cognizant of this work.

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