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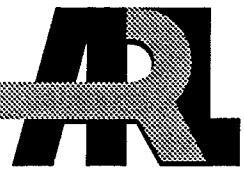

U.S. Army Workshop on Solid-Propellant Ignition and Combustion Modeling

by Martin S. Miller, Robert W. Shaw,
and David M. Mann

ARL-TR-1411 July 1997

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U.S. Army Workshop on Solid-Propellant Ignition and Combustion Modeling

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Abstract

A workshop with the objective to view the current state of the art of energetic-material combustion models within the context of future requirements of gun interior-ballistics (IB) models was held at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground, MD, on 9 and 10 April 96. The workshop was motivated by the recognition that modeling and simulation will be an essential cost-saving and time-saving tool in the design, development, testing, and evaluation of future gun-propulsion systems, and that, under current funding constraints, research on the underlying fundamentals must be carefully directed toward the most critical technology barriers. To facilitate this process, a perspective was presented on the fundamental physics and chemistry currently utilized in IB codes (XKTC, etc.) and the extensions planned for advanced codes (the NGEN family). The state of the art in fundamental descriptions of energetic-material combustion was then summarized and discussed with the intent of giving focus to those issues that could impact the future development needs of the IB research community.

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EXECUTIVE SUMMARY

A workshop with the objective to review the current state of the art of energetic-material combustion models within the context of future requirements of gun interior-ballistic models was held at ARL, Aberdeen Proving Ground, MD, on 9 and 10 April 96. The workshop was motivated by the recognition that modeling and simulation will be an essential cost-saving and time-saving tool in the design, development, testing, and evaluation of future gun-propulsion systems and that, under current funding constraints, research on the underlying fundamentals must be carefully directed toward the most critical technology barriers. To facilitate this process, a perspective was presented on the fundamental physics and chemistry currently utilized in interior-ballistic codes (XKTC, etc.) and the extensions planned for advanced codes (NGEN family). The state of the art in fundamental descriptions of energetic-material combustion was then summarized and discussed with the intent of giving focus to those issues which could impact the future development needs of the interior-ballistics research community.

The future of gun propulsion is being influenced by several trends, including concepts which would replace some or all of the chemically bound energy with electrical energy. However, careful examination shows that a solid-propellant-based gun system continues to be attractive because (1) a solid material is a proven, stable, and volume-efficient means to store energy, and (2) the solid can be tailored to release this energy in a controlled and reproducible manner. New energetic materials with increased impetus and energy are not only possible but on the horizon. However, this increased energy density, by itself, will not achieve the performance goals being set for future systems. Meeting these goals will also require a significant increase in loading density, i.e., the energetic material will occupy a larger fraction of the combustion chamber volume. In a high-loading-density configuration, there is extremely limited free volume available for efficient flamespreading. Laboratory experiments suggest that these narrow passageways are capable of supporting behavior varying from flame quenching to a high-speed flame-propagation mode. Such divergent phenomena are the result of a competition between heat-transfer and chemical-reaction rates. Also, recent gun-simulator work has shown that the unusually long ignition delays sometimes exhibited by nitramine composite propellants can likewise be traced to a competition between convective heat transfer and finite-rate energy release by reactions at low pressure. Thus, in high-loading-density charge configurations, one can expect increased sensitivity of interior-ballistic events to factors such as dimensional tolerances and variations in igniter functioning, carrying with it the risk of unexpected and catastrophic pressure-wave formation. A thorough knowledge of the fundamental interaction between flow physics and finite-rate chemical reactions is therefore crucial to constructing the submodels required for future interior ballistic codes. In the higher performance systems of the future, the ability of IB codes to predict the consequences of these highly coupled, nonlinear processes will prove essential to identifying and correcting potentially hazardous propelling-charge configurations.

Understanding the essential physics and chemistry of propellant combustion is a daunting task, but enormous progress has been achieved over the last decade. As an example of both the complexity and the progress, note that two separate gas-phase reaction stages exist for most propellants. A reasonably sound description of the ignition delay associated with the second stage alone (dark zone) has now been developed and utilizes dozens of chemical species and hundreds of reactions. Kinetic mechanisms for the primary flame are more difficult to validate but are already receiving significant attention. Detailed-kinetics, steady-state combustion models have been developed (for single ingredients only, so far), and these can serve as frameworks for identifying and assessing more subtle phenomena than could be included at first. A first-generation model also now exists for probing time-dependent phenomena such as ignition and transient combustion. Descriptions of condensed-phase reactions and interphase phenomena will continue to challenge the research community, but new theoretical chemistry tools such as density functional theory are beginning to enable Monte-Carlo and molecular-dynamics descriptions of these previously intractable problems. The long-standing goal of predicting the burning rate of a propellant from its ingredients now appears to be reachable in the foreseeable future. Such a capability would truly revolutionize the development of new propellants.

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1. INTRODUCTION

A workshop with the objective to review the current state of the art of energetic-material combustion models within the context of future requirements of gun interior-ballistics (IB) models was held at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground, MD, on 9 and 10 April 96. The workshop was motivated by the recognition that modeling and simulation will be an essential cost-saving and time-saving tool in the design, development, testing, and evaluation of future gun-propulsion systems and that, under current funding constraints, research on the underlying fundamentals must be carefully directed toward the most critical technology barriers. To facilitate this process, a perspective was presented on the fundamental physics and chemistry currently utilized in IB codes (XKTC, etc.) and the extensions planned for advanced codes (NGEN family). The state of the art in fundamental descriptions of energetic-material combustion was then summarized and discussed with the intent of giving focus to those issues which could impact the future development needs of the IB research community. The structure and goals of the workshop were determined by a joint effort of the Army Research Office (ARO) and ARL scientific staff. A list of the participants is given in section 9.

Though IB modeling provided the context for the present workshop, it is also recognized that development of models that could predict *a priori* the burning rate of a hypothetical substance from its ingredients would revolutionize the development of new or special purpose propellants. Even partial avoidance of the presently necessary and onerous tasks of synthesizing new materials and measuring burning rates and other properties would be of obvious economic and operational value. Thus, this report provides a useful documentation of the general state of the art in such models and where further development effort is indicated to attain this desirable goal.

It is worth noting that, while various weapons concepts may come and go in the struggle to maintain the superiority of U.S. forces, one can predict with virtual certainty that these weapons systems will always employ energetic materials in the capacity of explosive or propellant. As systems are pushed to higher and higher performance levels, the traditional cut-and-try methods of development may consume inordinate resources or simply fail. A sophisticated grasp of nuances in the fundamental processes involved in energetic-materials combustion then may well prove to be essential to success. A clear case for long-term support of fundamental research in this area is thus not difficult to make. Through workshops such as this, it is hoped that methodical scientific progress can be coupled with useful near-term systems benefit.

The workshop was structured as follows. The first day was devoted to extended presentations designed to lay out the IB issues and transition to a critical assessment of the current state of detailed combustion modeling. Discussion of the interrelationship among these topics and attempts to achieve consensus on the important technical barriers occupied the allotted time (about four hours) on the second day. Research recommendations from that discussion are

preserved in this report, which, we hope, will be helpful in planning future Army research on the combustion of energetic materials.

The formal presentations along with the respective topical focus of each are outlined as follows:

1. Current directions in Army gun-propulsion systems (concepts and actual weapons systems) driving the further development of IB models. Approach to the development of next-generation IB models (i.e., NGEN family of codes). Identification of fundamental combustion phenomena whose descriptions may be needed by NGEN. Assessment of the level of detail which can reasonably be expected to be incorporated into NGEN for ignition and combustion phenomena. (Dr. Douglas Kooker, ARL)
2. Review and critical analysis of the chemical kinetics mechanism and rate data currently used to describe the gas-phase combustion chemistry and techniques for reduction of the full chemical-kinetic mechanism to the level of IB-code tractability. (Dr. William Anderson, ARL)
3. Discussion of the near- and far-term strategy developed at ARL for modeling finite-rate chemistry in IB models. Identification and discussion of untested assumptions implicit in current combustion models as developed from a study of the frozen-ozone prototype. (Dr. Martin Miller, ARL)
4. Review of the current status of the Penn State one-dimensional, multiphase, detailed-kinetics combustion model for RDX and status of its extension to nitramine composite propellant. Includes discussion of approximations, parameterizations, and data required as input. (Prof. Vigor Yang, Penn State)

In the following pages a short narrative has been prepared by each presenter describing the content of his oral presentation. In addition Prof. Kenneth Kuo of Penn State was asked to give a description of a single and multiple bubble model which is to be eventually incorporated into the Penn State comprehensive model to describe the two-phase subsurface region. This is followed by a summary of the discussion period.

This workshop was purposely limited to Army-sponsored research in order to keep the discussion tightly focused on uniquely Army problems. There was no intention to slight the research sponsored by other service branches. In this connection we here acknowledge the detailed models of RDX combustion that have been developed by Prasad, Yetter, and Smooke[1] and Davidson and Beckstead.[2] These models are similar in spirit and in level of detail to that developed at Penn State so that the discussion of the state of the art of combustion modeling applies to them as well.

1.1 References

1. K. Prasad, R. A. Yetter, and M. D. Smooke, "An Eigenvalue Method for Computing the Burning Rates of RDX Propellants," Yale University Dept. of Engineering Report ME-101-95, July 1995.

2. J. Davidson and M. Beckstead, "Improvements to RDX Combustion Modeling," AIAA Paper 96-0885, 34th Aerospace Sciences Meeting and Exhibit, Reno, NV, January 15-18, 1996.

2. FUTURE DIRECTIONS IN ARMY GUN PROPULSION AND INTERIOR BALLISTIC MODELING

Douglas E. Kooker, Army Research Laboratory

2.1 Background

Maintaining battlefield superiority during the next 20-25 years will require engaging enemy forces at greater range as well as defeating ever more sophisticated armor. For a projectile-based system to accomplish these objectives, the ability to deliver more kinetic energy from the launch platform will be required. Although the design of a future combat vehicle or system has not been finalized, potential delivery systems include an electromagnetic (EM) launcher and an electro-thermal-chemical (ETC) gun system. The EM launcher would not employ chemically stored energy, but there are many other difficult challenges presented by the physics. For the ETC gun system, a very significant fraction (>95%) of its muzzle velocity is to be derived from chemically stored energy, although the focus of the proposal usually highlights the electrical energy addition. Furthermore, underlying the advertised performance of the ETC gun is the assumption that this chemical energy can be packaged at high volume density and then released in a controlled and reproducible manner. Fulfilling this promise will require overcoming many challenges to current technology, which will be possible only with improved understanding of the physics.

As a brief background, early designs of electro-thermal (ET) guns envisioned electrical energy simply deposited into an inert "working fluid," which would then do the pressure-volume work on the projectile. The attractiveness of this concept wilted considerably after computation of the magnitude of the required power supply. The necessity to reduce the size of the power supply led to the concept of an energetic working fluid or liquid propellant (LP) and hence the concept of an LPETC gun. However, since this design adopts many features of the bulk-loaded LP gun, the LPETC system must confront similar problems—how to ignite and burn the LP in a controlled and reproducible manner. Increasing the viscosity of the liquid or going to a slurry (solid particles suspended in a liquid) may have the potential for better control of the burning surface area, which is crucial to limiting pressure excursions in the combustion chamber. The need to control the burning surface area seems to have fostered the idea of replacing the liquid with a solid propellant, creating the gun system known as SPETC. The attractiveness of a controlled progressive surface area along with an inherent ability to store energy efficiently will likely sway the decision in favor of SPETC.

The SPETC gun system, as with any gun, is volume limited. Hence, to a great extent, increased performance depends upon increased energy density per unit volume of combustion chamber. Since practical considerations currently limit electrical energy addition to 1 MJ or less, the increased energy density must be supplied by the solid propellant. Two options are available—increasing the chamber loading density (packing more propellant into the chamber volume) and/or employing a propellant with greater energy per unit mass [1]. With respect to the latter, the impetus of JA2 propellant is 1165 J/g, and its energy density is 4900 J/g {energy =

impetus/(gamma-1)}. A realistic goal for advanced tank-gun propellants is a modest increase of 20%; thus, an impetus of 1300 - 1400 J/g, with an energy of 6000 J/g. And, of course, mass density must be at least that of JA2, i.e., 1.6 g/cm^3. However, successful development of this energetic material (e.g., see Juhasz et al. [2]), by itself, will not deliver the desired performance. A significant fraction of the projected performance must be derived from an increase in loading density. The SPETC direct-fire application assumes a value of 1.25 grams of propellant per cubic centimeter of chamber volume or higher (at present, typical values are 0.9 g/cm^3). In such applications, the propellant may be formed into various slab geometries, instead of cylindrical grains or sticks. At these loading densities, less than 20% of the chamber volume will be available for igniter components and flow paths for igniter products. The limited porosity available in such a system will translate into extreme sensitivity to any deviations or excursions in the transient combustion process. Mild difficulties in the ignition process could quickly lead to the formation of catastrophic pressure waves.

The projected SPETC performance also assumes elimination of the temperature sensitivity of solid propellant burning rate, i.e., the fact that the solid burns at a slower rate at lower ambient temperatures. As a result, the propelling charge is designed to produce the maximum safe pressure for the gun tube when the ammunition is at the highest operating temperature; at lower ambient temperatures, system performance is reduced. Although energy addition to the chamber at lower temperatures may be able to compensate [3] for the inherent lower performance, there is no current evidence that plasma addition actually alters the low-temperature burning rate of the propellant. However, plasma/propellant interaction is an ongoing topic of research [4,5]. There are also a number of proposals to eliminate the influence of temperature sensitivity by heating the ambient propellant to the maximum temperature of the design. One idea is application of a microwave energy field [6] to raise the temperature of the ammunition just before it is fired.

Separate from ETC development, plans for future artillery systems have embraced laser ignition of solid propellant [7,8], a mode of ignition which is clearly compatible with the concept of a digitally controlled battlefield. To facilitate the laser ignition concept, future solid propellants need to be compatible with and easily ignited by laser radiation.

Design of future ammunition will also rely heavily upon the use of rigid combustible cases, which are typically constructed from compacted/compressed NC-based energetic material. Direct-fire systems, for example, will employ these materials in a continuing effort to reduce "discard" weight (the portion of the case/igniter material remaining after payload launch). In a similar fashion, achieving the range, zoning, and rate-of-fire requirements placed on future artillery systems will likely be possible only with ammunition packaged in combustible containers handled by an autoloader system. An example would be the 155-mm system based on the Modular Artillery Charge System (MACS) under development by PM-Crusader [9]. Proper functioning of the autoloader will mandate a combustible case material with a certain minimum mechanical strength. Furthermore, the thermal ignition threshold of this material must be sufficiently high to minimize or remove the threat of inadvertent ignition ("thermal cook-off") when a round is chambered into a hot weapon and there is a delay in acquiring the next target.

These properties have unintended but important implications in the area of ignition. The combustible case elements of the MACS system, for example, play a critical role in the early ignition and flamespreading behavior. Before an element ruptures (or burns through), it effectively isolates the enclosed solid propellant from the hot igniter/combustion gases flowing just outside. The rigid case material will, however, transmit mechanical forces and loads, which might easily transport the entire element to a different location in the chamber. The timing and location of case fracture-rupture and/or burn-through, particularly with respect to the functioning of a central igniter core, will have a great influence on the outcome of the transient combustion event—and hence the safe operation of the weapon.

To summarize up to this point, the future of gun propulsion is being influenced by several trends. A solid-propellant-based gun system continues to be attractive because (1) a solid material is a stable and volume-efficient platform to store energy, and (2) the solid can be tailored to release this energy in a controlled and reproducible manner. New energetic materials with increased impetus and energy are not only possible, but on the horizon. However, the requirement to maximize energy per unit volume will force applications in future systems at high loading density, which presents a great danger of combustion-driven pressure oscillations. Thus, new high-energy propellants should exhibit ease of ignition and controlled flamespreading, and possess robust mechanical properties (e.g., resistance to grain fracture—especially at low temperatures). In addition, a host of gun-system "compatibility" issues will influence the selection and development process. A prerequisite will be compatibility with rigid combustible cases. Other desirable features include ease of ignition with plasma and laser radiation, insensitivity to thermal cookoff, long-term storage compatibility with energetic liquids (to form a slurry), and possibly good absorption properties in the microwave frequency band.

2.2 Interior Ballistic Models

Models of the interior ballistic (IB) process have steadily evolved from closed-form solutions (e.g., [10, 11]), to lumped-parameter computer codes (e.g., [12, 13]), through more recent efforts (e.g., [14, 15]) based on a two-phase mixture theory which allows a description of ignition and flamespreading, as well as combustion-driven wave motion in the chamber. There is credible evidence that each proposal for a new propulsion concept seems to foster the development of a new IB computer code [16]. The present-day environment of diminishing financial resources virtually mandates a different approach. There is considerable redundancy as the various IB models address common problems of input, output, grid generation, enforcement of boundary conditions, as well as ensuring the balance of mass, momentum and energy. These aspects transcend the type of gun system. Could one computer model be constructed with enough flexibility and modularity to simulate the IB cycle for each of several different propulsion concepts? Given some general constraints on a possible weapon system, would it be possible to compare the predicted performance among several different propulsion modes? This is the ultimate objective behind development of the ARL "next-generation" (NGEN) interior ballistic code [17-22]. As stated by Gough [23],

"The guiding principles for the development of this code have been:

(1) applicability to all gun propulsion systems via the choice of suitable constitutive laws and input data;

(2) simplicity of code structure and numerical algorithms to promote portability to various computer architectures, particularly massively parallel systems;

(3) efficient solution algorithms which permit simulations to be completed in acceptably short times on a high performance work station."

Although NGEN is under continuous development, the heart of the code is a general form of the multiphase conservation or balance equations which are assembled and solved within a modular framework. Various constitutive relationships are available in subroutine libraries which can be accessed by the modeler to construct the solution to a particular problem. Nusca has demonstrated the power of this modular construction by simulating:

- a tank gun with projectile afterbody protruding into a chamber filled with combinations of solid propellant in granular, wrap/slab, and stick geometries [22, 26],
- an artillery cannon containing multiple increments filled with granular solid propellant [22, 26],
- a tank gun with ETC/plasma igniter [24],
- a plasma igniter functioning in a chamber filled with compressible inert liquid [24], and
- a plasma igniter functioning in air [27].

It is beyond the scope of this article to provide a summary of the balance equations, boundary conditions and numerical integration procedures employed within the NGEN model. However, the reader can find these details in various publications [16, 18-20, 23]. It may be useful, however, to review the basic philosophy behind the structure of the code. For the sake of argument, consider the problem of simulating the IB cycle of a direct fire weapon system employing a propelling charge with granular solid propellant. This propelling charge might contain 8000 propellant grains, each with 19 internal perforations. For the numerical solution to provide even a rough approximation to the transient 3-D "micro"-flow field at the grain level (including reacting turbulent shear layers, etc.) would require a grid system of staggering proportions; this problem is not tractable now, or even in the near future. An alternative approach is to "average" the complexities at the micro scale by applying a space-time averaging procedure over length and time scales which are large compared to changes in the micro flow. The formal averaging process produces a mixture theory [14] in which the dependent variables are the average values of the micro-flow properties. A fundamental decision in the NGEN development was to adopt this "macroscopic" description of a multiphase mixture. Clearly, then, the NGEN model is not designed to resolve the reacting flow field surrounding a 100-μm-diameter droplet of liquid propellant, or the details within a 50-μm-thick primary flame zone anchored at the gas-solid interface during combustion of a solid propellant. In effect, this type of detail contracts to a boundary condition between the gas and solid phases or is embedded in the

constitutive theory describing the interaction between the phases. The prescriptions assigned to phase interaction terms such as drag, heat transfer and energy release can easily play a dominant role in the simulation of the IB cycle. The NGEN formulation does distinguish between a continuous phase (e.g., mixture of gases and possibly small-diameter condensed phases in mechanical equilibrium) and a discrete phase (e.g., large solid grains, inert or energetic packaging elements), which are treated separately in the numerical integration procedure.

As discussed earlier, the rigid combustible containers used to enclose various geometries of solid propellant play an important role in interior ballistics. A goal for the NGEN code is to be able to (a) assign constitutive properties to the case material, and then (b) explicitly track the motion of the finite-thickness containers, as well as the (larger) fragments after rupture. This is an ambitious undertaking requiring considerable development; however, an interim solution which monitors a simple "burst strength" of the case walls has shown some promise [26]. The high-loading-density direct-fire configurations involve multiple segments of slab-type solid propellant. Although container boundaries are not usually an issue here, these segments can exhibit very nonlinear and nonisotropic behavior which must be described to the phase interaction terms in NGEN's macroscopic formulation. The simulations are indeed sensitive to these descriptions. Depending upon the type of propellant and geometry, it is entirely possible that these examples or future IB problems will require accurate submodels in the area of turbulence, or worse yet, the interaction between turbulence and multispecies reacting flow. NGEN would need considerable help here, as these are currently open research issues.

In most cases, the accuracy of the IB simulation is hostage to the level of detail built into the various physical submodels. Some of these submodels can be rather elementary. However, decisions about what benefit will follow from a given improvement need careful thought. Consider the typical description of ignition and combustion of a solid propellant. Convective heating establishes a transient thermal wave in the unburned solid which is assumed to be an inert material; ignition is declared when the surface temperature reaches some specified threshold value. At ignition, it is assumed that full combustion begins immediately, i.e., final equilibrium combustion products flow away from the propellant surface which is regressing at the steady-state rate dictated by the local value of pressure. In spite of the severe limitations inherent with this description of ignition and combustion, there have been many successful simulations of IB cycles where the IB code identifies the root cause of serious pressure oscillations (e.g., the Navy 5in./54 system, [28]) -- and gun testing has validated the result. Reflecting on these results suggests that a comprehensive and difficult upgrade to the combustion submodel (e.g., addition of a large finite-rate chemical decomposition mechanism to describe the gas-phase flame region) would produce virtually no improvement in the predictions for these particular ballistic problems. The explanation is straightforward. Above some modest value of pressure (probably around 20 MPa), the rates associated with the finite-rate gas-phase chemistry are much faster than the rate at which pressure disturbances can be propagated in the flow field; hence, the chemical rates are not the controlling process and in the simulation, might as well be infinite.

On the other hand, IB models employing the simple ignition and combustion submodels above have failed to predict delayed ignition sequences observed in a number of solid propellant weapon systems, particularly those with nitramine composite propellants. The problem is virtually impossible to isolate with data from gun firings. However, a special laboratory device

was designed in [29] to examine the convective ignition behavior of five different propellants under nearly identical flow conditions. Ignition delays for M10, JA2, and M30 were observed to be a few milliseconds; however, the nitramine composite M43 (energetic binder) showed time delays in the range of 250 ms, and XM39 (inert binder) exhibited delays over 600 ms. The data also suggest an inverse dependence on pressure, which would be consistent with the hypothesis that gas-phase chemical reactions are controlling chamber response. When the chamber configuration is altered to promote a rapidly rising pressure field, ignition delays for both nitramine propellants are reduced to less than 1 ms. The explanation offered in Kooker et al. [29] is "that convective ignition of nitramine composite solid propellant is significantly influenced by the low-pressure flame zone structure together with the slow burning rate. Before the final flame zone has a chance to form, the partially-reacted pyrolysis products evolving from the propellant surface can be swept away into a cooler part of the chamber, i.e., a Damkohler number argument." Preliminary IB simulations of this convective ignition event strongly suggest that the propellant combustion model must account for the finite-rate chemical decomposition associated with pyrolysis and transition to final flame products. At low pressure, the finite-rate chemical decomposition process is probably rate controlling.

In principle, an IB code can couple the important multiphase convective flow with a large multispecies finite-rate chemical decomposition mechanism. In reality, however, the problem is not tractable without a "reduced" reaction set based on a small number of species. Section 3 by Anderson addresses the many problems associated with establishing a complete reaction set to describe the propellant dark flame zone, and then shrinking this to a reduced set and verifying its accuracy. Another important quantity needed by the macroscopic formulation in NGEN will be a description of the reactive species entering the gas-phase region. Recall the earlier mention of thin zones which cannot be resolved (for reasons of numerical feasibility) and, instead, are collapsed into surface boundary conditions. The primary flame zone anchored to the solid propellant surface must be treated in this fashion. Hence the species concentrations which actually exit the primary flame zone of the solid propellant must be prescribed as a burning surface boundary condition to the NGEN code. Determining these boundary conditions and prescriptions for the other phase interaction terms represents an important contribution to the NGEN modeling effort.

2.3 References

1. McElroy, H. A., Buzzet, J. G., Schmidt, E. W., Rothgery, E. F., Greig, J. R. and A. A. Juhasz, "Alternate Electrothermal-Chemical (ETC) Propellant Study", ARL-CR-297, U.S. Army Research Laboratory, April 1996.

2. Juhasz, A. A., Robbins, F., Moy, S., Manning, T., Hartwell, J. and R. Wardle, "Energetic TPE Gun Propellant Characteristics, Ballistic Potential, and Recommended Research", ARL-TR-1239, U.S. Army Research Laboratory, November 1996.

3. Perelmutter, L., Sudai, M., Goldenberg, C., Kimhe, D., Zeevi, Z., Arie, S., Melnik, M. and D. Melnik, "Temperature Compensation by Controlled Ignition Power in SPETC Guns", 16th International Symposium on Ballistics, 23-28 September 1996, San Francisco, CA.

4. Del Guercio, M., Stobie, I. and W. Oberle, 'The Effect of Delayed Plasma Injection on the Combustion Characteristics of Solid JA2 Propellant", ARL-MR-322, U.S. Army Research Laboratory, July 1996.

5. Woodley, C. R. and S. Fuller, "Apparent Enhanced Burn Rates of Solid Propellants Due to Plasmas", 16th International Symposium on Ballistics, 23-28 September 1996, San Francisco, CA.

6. Howard, S. L., Chang, L.-M., Vong, T. T., Scannell, E. P., Kaplan, S. L., Tan, R. and C. R. Buffler, "Microwave Heating of Propellant: A Feasibility Study of a Conceptual Approach to Ballistic Improvement of Tank Ammunition", ARL-TR-1244, U.S. Army Research Laboratory, December 1996.

7. DeVries, N. M., O'Reilly, J. J., and B. E. Forch, "Laser Ignition of Energetic Materials Workshop", 30th JANNAF Combustion Meeting, CPIA Publication 606, Vol. I, pp. 191-203, November 1993.

8. O'Reilly, J. J., Lew, D., Forch, B. E., Newberry, J. E., Smith, D. C. and M. Todaro, "Laser Ignition System for Artillery", 32nd JANNAF Combustion Meeting, CPIA Publication 631, Vol. III, pp. 437-443, October 1995.

9. Cirincione, R., Chang, L., Hui, P. and J. Rutkowski, "Selection of MACS (Modular Artillery Charge System) for 155mm Artillery", 32nd JANNAF Combustion Meeting, CPIA Publication 631, Vol. III, pp. 381-390, October 1995.

10. Love, A. E. H. and F. B. Pidduck, "On Lagrange's Ballistic Problem", Philosophical Transactions of the Royal Society, Vol. 22, p. 167, 1922.

11. Kent, R. H., "Some Special Solutions for the Motion of the Powder Gas", Physics, Vol. 7, No. 9, September 1936.

12. Baer, P. G. and J. M. Frankle, "The Simulation of Interior Ballistic Performance of Guns by Digital Computer Program", BRL-TR-1183, U.S. Army Ballistic Research Laboratory, 1962.

13. Anderson, R. D. and K. D. Fickie, "IBHVG2 – A User's Guide", BRL-TR-2829, U.S. Army Ballistic Research Laboratory, July 1987.

14. Gough, P. S., "The Flow of a Compressible Gas Through an Aggregate of Mobile Reacting Particles", IHCR 80-7, Naval Ordnance Station, Indian Head, MD, December 1980.

15. Gough, P. S., "The XNOVAKTC Code", BRL-CR-627, Contractor Report to the U.S. Army Ballitic Research Laboratory, February 1990 {also see IHCR 80-8, December 1980}.

16. Gough, P.S., "Development of Next-Generation Interior Ballistics Code II. Applicability to Various Propulsion Systems," 31st JANNAF Combustion Meeting, CPIA Publication 620, Vol. 1, pp. 257-278, Oct. 1994.

17. Horst, A.W., Keller, G.E., and Gough, P.S., "New Directions in Multiphase Flow Interior Ballistic Modeling," BRL-TR-3102, U.S. Army Ballistic Research Laboratory Technical Report, May 1990.

18. Gough, P.S., "Formulation of a Next-Generation Interior Ballistic Code," 28th JANNAF Combustion Meeting, CPIA Publication 573, Vol. 1, pp. 321-337, October 1991.

19. Gough, P.S., "Development of a Next-Generation Interior Ballistic Code I. Evaluation of Computational Algorithms," 29th JANNAF Combustion Meeting, CPIA Publication 593, Vol. 1, pp. 27-40, October 1992.

20. Gough, P.S., "Formulation of a Next-Generation Interior Ballistic Code," ARL-CR-68, U.S. Army Research Laboratory Contract Report, September 1993.

21. Nusca, M.J., "Comparison of Numerical Schemes for Solving Systems of Hyperbolic Differential Equations for the Next-Generation Interior Ballistics Code," 30th JANNAF Combustion Meeting, CPIA Publication 606, Vol. 1, pp. 223-239, November 1993.

22. Nusca, M.J., "Investigation of Solid Propellant Gun Systems Using the Next-Generation Interior Ballistics Code," 31st JANNAF Combustion Meeting, CPIA Publication 620, Vol. 1, October 1994, pp. 279-292.

23. Gough, P.S., "Modeling High Performance Tank Gun Charges with the Next-Generation Code NGEN" 32nd JANNAF Combustion Meeting, CPIA Publication 631, Vol. I, pp. 531-546, October 1995.

24. Nusca, M.J., "Further Investigation of Solid Propellant Combustion Phenomena Using the Next-Generation Interior Ballistics Code," 32nd JANNAF Combustion Meeting, CPIA Publication 631, Vol. I, pp. 547-564, October 1995.

25. Gough, P.S., "Modeling Arbitrarily Packaged Multi-Increment Solid Propellant Charges with the NGEN Code," 33rd JANNAF Combustion Meeting, Naval Postgraduate School, Monterey, CA, 4-8 November 1996.

26. Nusca, M. J., "Application of the NGEN Interior Ballistic Code to Solid Propellant Systems of Various Propellant Configurations", 33rd JANNAF Combustion Meeting, Naval Postgraduate School, Monterey, CA, 4-8 November 1996.

27. Katulka, G.L., Nusca, M.J., and K.J. White, "Plasma Modeling for Ignition and Combustion Control Applications in Ballistics," 33rd JANNAF Combustion Meeting, Naval Postgraduate School, Monterey, CA, 4-8 November 1996.

28. Robbins, F. W., Kudzal, J. A., McWilliams, J. A. and P. S. Gough, "Experimental Determination of Stick Charge Flow Resistance", 17th JANNAF Combustion Meeting, CPIA Publication 329, Vol. II, pp. 97-118, November 1980.

29. Kooker, D. E., Howard, S. L. and L.-M. Chang, "Convective Ignition of a Granular Solid Propellant Bed: Influence of Propellant Composition", 26th International Symposium on Combustion, Naples, Italy, 29 July - 2 August 1996.

3. PROPELLANT DARK ZONE CHEMISTRY: DETAILED AND REDUCED MECHANISMS FOR INTERIOR BALLISTIC APPLICATIONS

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This presentation dealt with gas-phase chemical mechanism development for interior ballistic (IB) modeling applications. It is believed the chemistry of the dark zone mixtures produced by propellants during the early flamespreading stages of the IB cycle in large-caliber guns plays a major role in determining gun ignition delay behavior (see section 2). A large difference in the behavior for nitrate ester (e.g., single and double base) and nitramine (e.g., those containing RDX or HMX) propellants has been noted in ballistic simulator experiments [1]. This difference is believed traceable to differences in the dark zone (DZ) mixture chemistry for these two major propellant types. (The dark zone is a nonluminous gaseous region formed under many conditions between the luminous secondary-stage flame and the propellant surface region.) In development of a model for such a chemically complicated mixture as that of propellant dark zones (six to eight major components are present on the initial mixture; see section 3.1), it is necessary for the prudent kinetics modeler to consider literally tens of molecular species and hundreds of reactions. This is the case because it is virtually impossible with such a complicated chemical network to be certain which reactions matter without full integration of the rate equations. In development of a detailed chemical network, one therefore attempts to be as comprehensive as possible, including all reactions which might conceivably matter to the starting mixture and species formed by subsequent reactions. One then performs calculations appropriate to the conditions of interest and dissects the results (chemical pathway and sensitivity analysis) to determine which reactions are most important for the mixture. The determination of which reactions are most important serves to determine which elementary-reaction kinetics parameters are deserving of special attention in development of the detailed mechanism; it also helps in later reduction of mechanism size. Because of computational limitations, it is not feasible to use the large, detailed mechanisms in computational fluid dynamical (CFD) models, such as IB codes currently being developed. We have, therefore, developed reduced DZ mechanisms for the two major propellant types.

The presentation was divided into six major sections. These covered the following topics: (section 3.1) definition of typical dark zone conditions and behavior; (section 3.2) flame chemistry in the propellant's near surface reaction zone which may affect whether a DZ forms; (section 3.3) physics and assumptions for a model of the DZ chemical structure; (section 3.4) description of the detailed DZ mechanism development; (section 3.5) comparison of DZ mechanism predictions to experiments; and (section 3.6) a general approach to reduced mechanism development for ignition delay problems and its application to DZ mixtures. For most of these sections, the author's notions of studies needed to improve accuracy or test the model are indicated. The major difficulty at present is the lack of precise experimental data taken under well-defined conditions to sufficiently test accuracy of the detailed chemical model. The model has been tested against available propellant strand burner data from those experiments where data on the DZ conditions are available. These data are used as initial conditions for a

time dependent chemistry model to predict ignition delay time. (The reader is warned here to note that although they are related, the chemical or DZ ignition-delay times to which we refer here are different from gun ignition delays. The latter are strongly influenced by flamespreading and physical effects as well as chemistry.) Delay times may then be compared with experimental results obtained from analysis of DZ length data and propellant burn rate. However, the data from strand burner studies on what initial conditions to use (temperature, pressure, mixture ratio, and even DZ length) are not nearly as well known as in typical kinetics experiments. This is the major limitation and uncertainty in the comparisons.

3.1 Typical Dark Zone Conditions and Behavior

In a typical strand burner experiment, a cylindrical strand of propellant is burned in a pressurized vessel with access for measurement diagnostics. Usually, a flow of inert gas around the strand is used to prevent the flame from propagating down the side of the strand. The temperature and majority species concentration profiles are fairly constant within the DZ. Typical pressures used are 5-40 atm (constant pressure vessel). Measured DZ temperatures range from about 1100-1600 K, depending primarily on propellant type. For nitrate ester propellants, measurements indicate the DZ majority species are H_2, NO, CO, CO_2, N_2, and H_2O. For nitramine propellants, all the preceding species and HCN are found in large quantity, plus traces of N_2O. We believe the traces of N_2O to be extremely important in determining DZ length. Traces of other species such as CH_2O, CH_4, and C_2H_4 have also been observed, but our best current detailed chemical model indicates these are unimportant and may be ignored. If a dark zone forms, it is well established that this results because of the low reactivity of the intermediate species HCN and NO. Formation of these species delays full chemical energy release. At the end of the dark zone, they are rapidly converted to products, resulting in higher concentrations of N_2, CO_2, H_2O, and perhaps H_2 and CO with the release of considerable chemical energy. The reactions of NO and HCN with most combustion species are slow. In the DZ, slow reactions lead to slow radical buildup until, at the end of the DZ, runaway reaction (ignition) suddenly occurs. Such delayed ignition behavior is common for hot, nonequilibrium mixtures. It is frequently observed, for example, in shock tube experiments on fuel/oxidizer mixtures. The DZ flame structure looks very unusual; but, although physical effects might well affect the length, the major underlying factor affecting length is undoubtedly the chemical ignition delay time. The length is primarily controlled by the delay time and convective rate of the DZ gases. Therefore, from the viewpoint of the kineticist, there is nothing at all qualitatively unusual in the DZ spatial structure. The major challenge is to understand the chemistry of these mixtures quantitatively. This topic has not received much prior study.

There is a tendency to focus attention on comparison of the predicted and measured DZ lengths as a primary judgement of model quality. It is quite easy to understand this tendency, because one's eye is readily drawn to differences in length of plateau regions of temperature and species concentrations, as in the DZ. Differences in absolute DZ temperature and concentrations draw less attention, but may be more indicative of major mechanistic errors such as a missing key reaction (or, even more insidious, inclusion of a key reaction but with much too low a rate constant). We have found that the predicted DZ ignition delays, and, hence, the lengths, are quite sensitive to the initial DZ temperature and mixture ratio. A 50-K temperature change can easily

change predicted delay (length) by a factor of two! It seems quite feasible to have the primary stage mechanistic features of a full propellant model be incorrect, leading to a very incorrect set of DZ leading edge conditions, yet also have compensating errors in the DZ chemistry leading to a misleading prediction of the experimentally observed length. One must keep in mind, in making the comparisons, that correctly predicting the leading edge DZ conditions, especially the temperature, is likely more important than obtaining the correct length.

3.2 Primary Flame Chemistry Leading to Dark Zone Formation

In this section, some chemical factors which could favor the formation of a DZ were briefly discussed. This led to some rather interesting discussion, and some dissension, because of the complicated chemical and physical factors which may affect first-stage propellant flames. Suffice it to say here that there was not complete agreement of the panel on these issues. The main viewpoints expressed here reflect the biases of the author, and may be somewhat naively simplified. They are, nevertheless, advanced for consideration.

Primary flame species and reactions which ultimately lead to NO or HCN as intermediates should favor formation of a DZ. It is the relative slowness of the subsequent reduction of NO to N_2 (and, in the case of nitramine propellants, reaction of HCN to final combustion products) which traps energy and results in the ignition delay, hence observation of a moderate temperature, nonluminous region.

In the case of nitramines, it is thought that formation of HCN/NO_2 (or perhaps HCN/HONO) intermediates is favored at relatively high temperatures in the condensed phases, while formation of CH_2O/N_2O intermediates is favored at lower temperatures. CH_2O and N_2O are fairly reactive and therefore are unlikely to survive the primary flame zone. The chemistry involving these species typically leads towards final products, e.g. H_2O, N_2, CO and CO_2, and not NO (and certainly not HCN). For example, under the rich conditions prevailing in propellants, the reaction

$$H + N_2O \rightarrow N_2 + OH$$

is the most likely fate of the N_2O. On the other hand, NO_2 or HONO tend to produce NO via the fast reactions

$$H + NO_2 \rightarrow NO + OH$$

and

$$H + HONO \rightarrow NO + H_2O\,.$$

Because of their low reactivity with most combustion species, once formed, HCN and NO will tend to survive the primary flame zone. Therefore, any favoring of the HCN/NO_2 decomposition pathway relative to CH_2O/N_2O is expected to increase the tendency to form a dark zone. However, complex and competing factors are involved. For example, higher temperatures also typically increase reaction rates. This tends to reduce the length of the DZ. Regardless of a high-

temperature shift in mechanism favoring production of NO_2, if the temperature is sufficiently high, the reactions could be fast enough that no DZ is exhibited.

For nitrate ester propellants (e.g., double base), little HCN is thought to form but NO_2 is the dominant oxidizer in the primary flame. Thus, double base propellants typically exhibit DZs. An exception is M30, which contains large amounts of nitrate esters and nitroguanidine. Because of its chemical structure, nitroguanidine is expected to produce large amounts of N, NH, or NH_2. This would disfavor DZ formation because of well-known, fast NH_x + NO reactions which lead ultimately to formation of final product N_2. It has been observed that M30 does not typically form a DZ.

At this point the workshop discussion turned slightly away from factors controlling whether a DZ forms to a related question on initial stages of the IB cycle in guns. Given that a propellant is known to burn with a DZ, can the propellant bed achieve uniform flamespreading from the primary flame alone? The ARL ballistician thought this is unlikely; the temperatures are too low. The secondary flame is needed. It was then suggested that perhaps what we need to do is seek to minimize the likelihood of formation of a DZ and, hence, reduce the chance of a significant gun ignition delay. While this could ultimately be a useful goal, most panel members felt that understanding the chemistry controlling the delay should be our immediate goal. Since the DZ appears to control the gun ignition delay, understanding why it forms (near-surface chemistry and physical effects) and its properties, especially chemistry, once formed should be the more immediate goal as opposed to ad hoc experiments to remove it. Propellants in use or development likely will be chosen for a variety of factors besides the formation of a DZ.

3.3 Physics and Assumptions of Dark Zone Model

Prior to presenting information regarding mechanisms to model propellant DZ structures, an outline of the simplifying physical assumptions made was presented. The first such attempt at modeling chemistry of the DZ was made by Sotter in 1965 [2]. Most of the assumptions made more recently in chemical models of the DZ were developed in his work. Until recently, nothing new along these lines was accomplished. Then, in 1990, Fifer et al. [3] rediscovered the significance of Sotter's early work and used much the same physical assumptions. However, they used much more updated chemistry, since 25 years of development of the nitrogen combustion chemistry database had passed. The mechanism used in that work was taken largely from Miller and Bowman (MB89) [4], with only a few significant modifications. Over the last 5 years, ARL and ARL/University of California at San Diego (UCSD) researchers [5-9] have further developed the chemical mechanism, including: (1) critical evaluation of the most sensitive DZ reactions from several prior propellant and DZ mechanisms; (2) development of reduced chemical mechanisms; and (3) continual updating of the mechanism for addition of newly discovered reactions, newer kinetics measurements on controversial reactions, and thermodynamics. Much the same physics description has been utilized throughout studies by these three groups.

The physical assumptions made in the model are: (1) The DZ flow is one-dimensional, laminar, and steady with no DZ area change. The one-dimensional and laminar assumptions are

likely excellent. The assumption that the propellant flame structure is steady is only fair since propellant flames in strand burners do flicker. (2) There is negligible diffusion or thermal conduction in the DZ. These assumptions would seem to be sound since the gradients in majority species and temperature profiles are small. (3) The initial conditions are taken from critical evaluation of strand burner experiments. Due to limitations in measurement techniques, there are no experiments which provide a full set of all the necessary data on conditions, DZ length, and burn rate. (4) There is a nearly constant flow velocity in the DZ. This should be a fairly good assumption since the species and temperature profiles plateau in the DZ. It does, however, depend on the constant area assumption. (5) The initial radical concentrations are negligible. Until recently, this assumption had been a major concern. However, the ARL/UCSD reduced-mechanism study has revealed that the radicals are rapidly forced into steady state in the DZ, and their steady-state concentrations are negligible. The assumption seems likely to remain true even if future developments indicate major changes in the detailed mechanism are necessary. (6) Pressure is constant, an excellent assumption. (7) The burn is adiabatic. Temperature measurements in the luminous flame zones of propellants indicate this is also an excellent assumption. These simplifying assumptions lead to:

$$\tau_d = L_d/v$$

where τ_d is chemical ignition delay, L_d is measured dark zone length, and v is the gas convective velocity. From the continuity relation for the interface region:

$$v = r\rho_s/\rho_g$$

where r is the propellant burn rate, ρ_s is the solid density, and ρ_g the density of the gaseous DZ mixture. Combining these equations and using the ideal gas law, one finds:

$$\tau_d = L_d MP/RTr\rho_s$$

where R is the ideal gas constant, M is the average DZ molecular weight, P is pressure, and T is temperature. ARL/UCSD researchers use a time-dependent homogeneous reactor model (SENKIN [10]) with constant pressure, adiabatic assumptions to compute ignition delays, and the ARL postprocessor [11] to analyze the chemical results. These codes allow model calculations to be performed to test sensitivity of results to the assumed initial conditions and rate constants.

The ARL/UCSD researchers decided upon discussions with their ARL ballistician colleague to expand the (P,T) region of interest beyond that of typical DZ conditions in strand burner experiments discussed above. It was thought that ranges of P = 1-30 atm and T = 1000 - 1800 K would cover those of interest to model the gun flamespreading and ignition delay phenomena. Both the detailed and reduced DZ chemical mechanisms have been developed with these limits in mind. The consequences of increasing these ranges are that the process complexity increases and the range is well outside that of available strand burner data so that few, if any, verification experiments are available for testing. This increases the risk of major error, including the possibility of entirely missing important reactions.

3.4 Detailed Mechanism for Double Base and Nitramine Dark Zones

The most current version of the detailed chemical mechanism utilizes about 40 species and 200 chemical reactions. This mechanism has been developed over the last five years [5-9]. The mechanism has been heavily influenced by the aforementioned benchmark review on nitrogen chemistry in combustion, MB89 [4]. Most of the hydrocarbon (HC) chemistry, except for CH, is not included. Hydrocarbon chemistry appears unimportant for the low levels observed (~1%). But a potentially significant reaction type, about which little is presently known, is RH + NO = R + HNO. In early tests of the model, $CH_4 + NO = CH_3 + HNO$ was included (using an upper limit estimate to k based on a collisional A-factor and E_a equal to the enthalpy) but found to be unimportant for the low levels of CH_4 observed in the experiments. Since inclusion of HC chemistry would unnecessarily complicate and increase size of both the detailed and reduced mechanisms, all HC reactions except those of species CH have been removed. As previously mentioned, in early development of the mechanism [5], besides MB89, mechanisms from several other sources which had previously been used to model propellants (though not necessarily having modeling of the DZ as a primary goal) were considered. Because of the omission or inclusion of certain reactions, these mechanisms exhibited very different sensitivities to different key reactions when used to model the DZ. Critical literature reviews were performed in an effort to determine which are correct. Also, for two of the most important:

$$HNO+NO \rightarrow N_2O+OH$$

$$CO+NO \rightarrow N+CO_2$$

ab initio calculations were performed, at our behest, by our ARL colleagues. The first reaction was found to be the most important radical source (hence is the main reason ignition eventually occurs at the end of the DZ) for nitrate ester propellant DZs. The *ab initio* studies confirm the rate coefficient currently in use is reasonable, in agreement with more recent theoretical and experimental studies. The second reaction was also predicted in early studies to be a major source of radicals. But our critical literature review [5,9] quickly revealed the rate coefficient in use (obtained automatically by the computer codes using the reverse reaction from MB89) was grossly incorrect; and the reaction is spin forbidden so that we estimated it likely not fast enough to matter under any conditions of practical combustion importance. Later *ab initio* calculations estimating a minimum barrier height for the crossing point of the two electronic surfaces involved in the reaction indicate the reaction's activation energy must be very high, substantiating our estimate the reaction may be neglected. The earlier rate coefficient is so high that some researchers modeling DZs have been misled to believe that it is the most important radical source in all DZs. The situation was particularly insidious, because, using the reaction in the model, the agreement between predictions and experiment is excellent. However, given the simplifying assumptions used in the model and the rather wide error limits of experiment (see later), a much lower level of agreement (factor of 2-3) is acceptable. The ARL group's modeling results (unpublished) show the reaction orders, that is, the predicted global behavior of ignition delay as function of the starting mixture ratio, are strongly affected according to whether the reaction is included or not. Usage of the reaction is unacceptable for IB modeling, therefore, because it could lead to an incorrect prediction of trends for global responses in parametric studies.

A partial list of reactions reviewed for the detailed ARL DZ model is presented in Table 1. A detailed discussion and references are not presented here; see instead Anderson et al. [9]. An asterisk next to the reaction in the table indicates the reaction is (or might be - one must realize the rate coefficients for some of these reactions are poorly established) of importance to the DZ and also in need of further study. A few comments are made here and in the next section regarding a few of the reactions. In the following section some comparisons with available experimental data are very briefly discussed.

(1) $NH+CO_2 \rightarrow HNO+CO$ and $NH+H_2O \rightarrow HNO+H_2$.

The main products are probably not those presented; see next section.

(2) $CO+N_2O \rightarrow CO_2+N_2$.

If it is included, this reaction has an important sensitivity in DZ calculations. However, the range of the available rate coefficient expressions is very wide. Recent works indicate the rate coefficient must either be at the lower bounds of reported expressions or negligible. The lowest reported expressions when used in the ARL DZ model indicate the reaction has an important contribution for DZ mixtures at 1000 K. However, ARL's best estimate at present is to leave the reaction out. Clearly, further work is indicated.

3.5 Comparison of Detailed Mechanism to Experiment

In this section a brief description of comparisons of the ARL DZ model to available relevant experimental data is presented. Only a descriptive narrative is presented. A detailed report containing figures depicting the results is in preparation [9]. The discussion is divided into two subsections, one on carefully controlled kinetics experiments on DZ relevant mixtures, the second on strand burner experiments. It will be seen that, unfortunately, there is only scant experimental information available for testing the model.

3.5.1 Static Reactor Experiments on DZ Related Mixtures

The Emory University group has studied mixtures of H_2/NO and H_2/NO/CO [12]. The analysis of both that group's own and prior experimental studies on H_2/NO have led to the best presently available rate coefficient for the extremely important DZ reaction

$$HNO+NO \rightarrow N_2O+OH.$$

The most recent ARL model is in reasonable agreement with those results for both mixtures. ARL researchers [9] have found the H_2/CO/NO data are critically important to refute

Table 1. Partial List of Mechanistic Data Reviewed for Detailed ARL DZ Model.

Reactions: (Reactions marked with a "*" are in need of further study.)

	$N + CO_2$	→	$NO + CO$	
*	$NH + CO_2$	→	$HNO + CO$	
*	$NH + H_2O$	→	$HNO + H_2$	
*	$CO + N_2O$	→	$CO_2 + N_2$	May be important for DZ mixtures at low T.
*	$N_2O + M$	→	$N_2 + O + M$	Work needed on M = NO, CO, CO_2, H_2, HCN; but chemistry complex for M = fuel.
*	$HNO + NO$	→	$N_2O + OH$	The most sensitive reaction for double-base DZ over the entire expanded T,P range; also important for nitramine DZ.
*	$N_2O + NO$	→	$N_2 + NO_2$	Entire T range needs study; most of the relevant experiments in the literature have been misinterpreted; current expression used is from the ARL critical review, has wide error limits.
*	$NO + NO$	→	$N_2O + O$	Moderately sensitive for high T, low P double-base DZ; currently under study by ARL/Rensselaer Polytechnic Institute researchers.
	$NCO + NO$	→	products	
	$NCO + NO_2$	→	products	
	$CN + NO$	→	products	
*	HCN, HNC, HNCO reactions			
*	$HNCO + H$	→	$NH_2 + CO$	
	$NH_2 + NO$	→	products	Important, but NO_x community is studying. Appears recent works have settled issues regarding this reaction.
	$H + N_2O$	→	products	
	$OH + N_2O$	→	products	
*	$H_2 + NO_2$	→	$HONO + H$	
*	$HNO + H$	→	$NH + OH$	
	$2\,HNO + M$ and subsequent $(HNO)_2$ reactions.	→	$(HNO)_2 + M$	$(HNO)_2$ represents various HNO dimers. HNO dimers likely important only if IB codes must be extended below 1000 K. Presently, a need for such extension is unclear.

Thermochemistry reviewed and revised: Heats of formation of: NH, NH_2, HNO, CN, NCO, HNCO

measurements on two NH reactions suggested in recent publications. These reactions, mentioned in the prior section, are: $NH+H_2O = HNO+H_2$ and $NH+CO_2 = HNO+CO$. (The latter has appeared, with a different rate coefficient estimated by questionable methods, in one mechanism used in propellant-related modeling. See Vanderhoff et al. [5].) Measurements relating to these are given in Rohrig and Wagner [13]. The results that these reactions have appreciable rate coefficients are quite unexpected, because both reactions are spin forbidden. Furthermore, upon inserting the reactions into the ARL mechanism, predicted DZ ignition delays were so short that a DZ of any length could not possibly exist, a result in rather stark contrast with experiment. In the model, what happens is that the reactions reverse and form NH radicals causing ignition. This results and is a strong effect because HNO is always present in large amounts, for a trace species, in high-temperature mixtures containing high concentrations of H_2 and NO; two key reactions involving HNO are, roughly, partially equilibrated, leading to this situation [9]. However, one is always concerned in the case of testing the DZ mechanism against propellant data. The difficulty is that however unlikely it might seem, perhaps something about the exact nature of the starting DZ mixture is being missed in a rather important way. Carefully designed kinetics experiments do not have this difficulty (except in cases of high sensitivity of results to impurities). The ARL group has found upon testing against the Lin group's data on H_2/NO/CO that inclusion of either of these reactions causes predicted global reaction rates to be orders of magnitude too fast compared to experiment. Furthermore, the reaction $N+CO_2 = NO+CO$ was also tested, utilizing the MB89 rate coefficient. This also leads to predicted rates which are too fast (though not nearly so fast as the two previously mentioned reactions), thus lending further support to the previous conclusions the reaction should not be included.

The experiment of Rohrig and Wagner [13] was designed such that only the disappearance rate of reactants was measured, not product identities. The assignment of product channels was made based primarily on thermodynamics of possible product channels, and chemical intuition. ARL researchers believe the reaction rates are correct, but the products have been incorrectly assigned. Some alternative channels are discussed in Anderson et al. [9]. However, these possibilities have not been tested for compatibility with other experiments. It seems unlikely they would be important in the DZ mechanism because they do not involve HNO as product. However, these reactions also deserve further scrutiny.

The preceding results clearly indicate none of the three subject reactions should be included. They also demonstrate the crucial importance of experimental test data on mixtures approaching the DZ complexity and temperature conditions. Further data of this nature are highly desirable.

3.5.2 Strand Burner Experiments

In making comparison of DZ modeling predictions to strand burner experiments, it must be kept in mind that the experiment is inherently considerably less precise than the typical kinetics experiment. There are several sources of error which will be discussed in a moment. In spite of these difficulties, the data are extremely important for DZ modeling. These experiments provide the information about initial conditions to use. And, they provide at least a rough estimate of the correct DZ ignition delay time (length) for a steady-state DZ model. Since the DZ mixture measurements are so difficult, missing the initial conditions in an important way is a

considerable peril. Therefore, having the test data from actual propellant burns is crucial. The difficulties in DZ structural measurement are many: (1) The DZ temperature is typically known to within no better than 50 - 100 K. The model is quite sensitive to temperature uncertainties of this magnitude. Experiments show the initial DZ temperature, that is, near the DZ leading edge, increases by ~100 K as pressure increases from 5 - 30 atm. It is crucial to have the pressure-dependent initial temperature information. But the measurements get progressively more difficult as T increases, because the DZ length decreases. (2) The concentrations of species at the leading edge of the DZ are incomplete for all data sets. The concentrations of unmeasured species must be estimated by a combination of intuition and conservation of mass, atom ratios, and enthalpy. Error limits in the measured parameters makes the result rather imprecise. (3) The inert gas purge flow in the experiments could affect the DZ length and the expansion assumption made in the model. (4) The luminous flame in the strand burner experiments fluctuates. Severity of the problem is widely variable with propellant type. The experimentalist typically attempts to extract data from records in which the fluctuation has stabilized as much as possible. (5) There is a 25% observation error in DZ length even for burns in which the luminous flame position is relatively stable. (6) The relative error in measured DZ length is worse for higher P because the DZ length is smaller. (7) Many strands burn with a cupped surface which is not easily discerned unless the strand is extinguished and examined.

Given these many sources of experimental error in input data to the model, the predicted ignition delay has uncertainty limits of a factor of 2-3. The data needed for DZ modeling using the approach described in an earlier section are: (1) the burn rate at the pressure of interest; (2) the length of the DZ; (3) the DZ temperature, preferably measured at the leading edge; and (4) majority species concentrations, preferably at the leading edge. There are only a few data sets for which all the necessary data are available. These and the comparisons of theoretical and experimental ignition delays will be presented in detail in Anderson et al. [9]. Only the general evaluation of the ARL model is mentioned here.

Reliable data for nitrate-ester DZs includes two experiments which utilized a wide pressure variation, plus a few measurements at selected pressures from ARL researchers. One of the two works which included a pressure effect study yielded measurements of all the major DZ species we believe to be important except H_2O. (The lack of observation of H_2O is likely due to its condensation on sampling flask walls.) The H_2O concentration was inferred, albeit with rather wide error limits, from atomic conservation. Comparison of adiabatic flame temperature calculated using the resulting DZ mixture and measured temperature with that calculated starting with the solid propellant showed reasonable agreement. Thus, energy conservation is not violated. For the second experiment, the DZ mixture was assumed identical because no species measurements were performed. This seems reasonable because the propellants used in the two experiments were of very similar composition. Very good agreement, especially in slopes, is found for plots of calculated and measured ignition delays for both experiments in which pressure was varied. In comparison of results to *all* available experimental data, however, the calculated ignition delays are consistently about a factor of two larger than experiment. Although, as discussed above, this is actually good agreement, the ARL group finds the agreement can be made excellent by increasing the rate coefficient for

$$HNO+NO \rightarrow N_2O+OH$$

by a factor of 2. This increase is within error limits for that rate coefficient. The model is thus consistent with available nitrate-ester propellant data. Clearly, though, it would be valuable to have further, more complete data sets.

For nitramine propellants, there are even less data available. There is only one pressure-dependent data set, and the species concentration information is incomplete. Thus, the starting mixture composition was compiled from a number of sources. (The temperature was obtained from the original experiments.) Comparison of slopes of the ignition delay *vs.* pressure plots shows the modeled slope is about twice as steep as the experimental one. However, the agreement in slopes can be made excellent by increasing initial assumed temperature in the model by ~100 K at the low P end of the range and gradually smaller amounts toward the higher P end. This demonstrates the high sensitivity of modeling predictions to initial T for values within the precision limits of the experiments. As for the nitrate ester propellants, the predicted delay times for all experiments are about a factor of two larger than measured for all available experimental data. Changing the HNO+NO rate coefficient did not matter much here, because other reactions are more sensitive. However, the predicted delays are not nearly fast enough without assuming the presence of two percent of N_2O in the starting mixture. (The results are sensitive to this species because its insertion makes the radical source reaction $N_2O+M = N_2+O+M$ important.) This amount is at the upper end of measurement tolerances; but the tolerances are quite large (factor of two). Even more important, the predicted adiabatic temperature starting with the DZ mixture with the added N_2O is about 300 K larger than that starting with the solid propellant. This difficulty could perhaps be alleviated without greatly affecting predicted DZ ignition delays by keeping the high N_2O concentration, but lowering the assumed NO (thus increasing the equivalence ratio). This is an issue the ARL group hopes to pursue in the near future. In any case, the need for more complete datasets for nitramines is highlighted by the present observations.

In conclusion of this section, the following observations are made. The agreement of DZ ignition delay times between the ARL model and experiment is very good for nitrate ester propellants. The predicted adiabatic flame temperature of the starting DZ mixture agrees well with that of the solid propellant, as it should. However, although the model follows the available data, there are few data available for testing. For nitramine propellants, the agreement with experiment is only fair. It is not nearly as good as with nitrate ester propellants. The agreement can be improved by changing the initial temperatures, within error limits, and N_2O concentration. However, the adiabatic flame temperatures are too high. Further study of the initial conditions is needed to see if the flame temperature situation can be rectified. For both propellant types, there is a clear need for further test data, both from actual strand burner measurements and the cleaner, more carefully controlled kinetics experiments. In the case of strand burner measurements, careful attention should be paid to insure all the necessary test data, especially as many species concentrations as possible, are measured. Note, as mentioned earlier, the range needed for the IB model is 1000 - 1800 (and perhaps even lower), while the DZ temperature naturally occurring is 1100 - 1600. Additionally, note the DZ temperature for a given propellant type over its pressure range in strand burner experiments only varies within about 100 K within the 5-40 atm range, if at all. There is little control over how much the DZ temperature can be varied in strand burner experiments. Kinetics experiments on mixtures approximating the DZ mixture complexity would

provide data that is crucial for the testing of the initial temperature response of these mixtures.

3.6 Reduction of the Detailed DZ Mechanism: UCSD/ARL Reduced Mechanisms

As mentioned previously, the full detailed mechanism is too unwieldy for parametric IB modeling studies of gun ignition delays. For this reason, the UCSD/ARL group collaborated to reduce the detailed mechanism for use in IB modeling. Because the DZ mixtures for nitrate esters and nitramines are very different, the reactions important to each differ. Therefore a reduced mechanism was developed for each of these two major propellant types. The detailed mechanism consists of 42 chemical species and about 200 reactions. For each propellant DZ type, the reduction was effected in two steps: (1) A skeletal mechanism, still utilizing elementary reactions, was developed by removing unimportant species and reactions. This effort was greatly facilitated by pathway and sensitivity analyses. (2) Reduced mechanisms were then produced from the skeletal mechanisms by making the steady-state assumption on all trace species for which the assumption was reasonable. Both the skeletal and reduced mechanisms were thoroughly tested for accuracy in reproducing predictions of the detailed mechanism over the temperature and pressure range of interest in IB modeling.

For nitrate-ester propellants, UCSD/ARL has published [8] skeletal and reduced mechanisms based upon 15 species and 22 elementary reactions. Of the species, in the reduced mechanism seven of these (H_2, NO, N_2, CO, CO_2, H_2O, N_2O) are finite rate, while eight (N, NH, HNO, HONO, H, OH, O, NO_2) are placed in steady state. The reduced mechanism may then be represented by three global steps:

$$2\,NO + H_2 \rightarrow N_2O + H_2O \qquad \text{I}$$

$$N_2O + H_2 \rightarrow N_2 + H_2O \qquad \text{II}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{III}$$

Predicted ignition delays using the skeletal and reduced mechanisms have an average error of about 5%, and a worst-case error of about 10%, over the T,P range of interest in IB modeling.

For nitramine propellants, UCSD/ARL [8] produced skeletal and reduced mechanisms based upon 17 species and 23 elementary reactions. Of the species, in the reduced mechanism ten (H_2, NO, CO, CO_2, N_2, H_2O, HCN, N_2O, H, HNCO) are finite rate, while seven (NH, HNO, HNC, NH_2, NO_2, OH, O) are placed in steady state. The reduced mechanism may be represented by six global steps:

$$2\,NO + 2\,H_2 \rightarrow N_2O + 2\,H + H_2O \qquad \text{I}$$

$$H_2O + HCN \rightarrow H_2 + HNCO \qquad \text{II}$$

$$N_2O + 2\,H_2 \rightarrow N_2 + 2\,H + H_2O \qquad \text{III}$$

$CO + H_2O$	$\rightarrow$	$CO_2 + H_2$	IV
$2\,H + M$	$\rightarrow$	$H_2 + M$	V
$NO + H + HNCO$	$\rightarrow$	$N_2O + CO + H_2$	VI

Predicted ignition delays using the skeletal and reduced mechanisms have an average error of about 15%, and a worst case error of about 30%, over the T,P range of interest in IB modeling.

Since the development of the reduced mechanisms presented in Ilincic et al. [8], an update to the detailed mechanism has revealed that three additional reactions and two additional species, HNNO and NNH, are important and must be included in the skeletal and reduced mechanisms for both propellant types. New skeletal and reduced mechanisms have therefore been developed and will be presented in a future publication [14]. Curiously, both of these species may be placed in steady state, resulting in reduced mechanisms which may be represented by identical global reactions to those above. The ignition delays in the low T, high P region of the parameter space of interest for IB modeling, however, are considerably lower (up to a factor of three) for the updated mechanisms. This result highlights the need for kinetics data to further test the mechanism.

Several other ways were discussed in which the detailed mechanism might be reduced for use in IB modeling. These include: (1) A variation on the above approach was suggested: remove unimportant rate terms in the reduced mechanism conservation equations to speed calculations. Careful attention would have to be paid to insure mass and energy conservation is preserved by this approach. (2) Asymptotic analysis could provide closed-form rate expressions for the global reactions. (3) A single-reaction-fit approach might provide a global reaction and rate-constant expression. Some doubts were expressed, though, as to how well this might be expected to work. (4) A multiple-global-reaction approach, which is rather ad hoc but effective, has been used by Fifer [15] to develop simple reduced mechanisms of only a few reactions for DZs. Unfortunately, it was based on a detailed mechanism now known to contain an important, incorrect reaction. What is attractive about this ad hoc approach is that, like (2), it provides closed-form rate expressions.

3.7 Conclusions

At the conclusion of the presentation, several ideas regarding future work that would be desirable were presented and discussed. These, and some mentioned earlier, are summarized here.

Ballistic simulator flamespreading experiments could be performed with sampling prior to ignition to compare with gas-phase DZ species observed in strand burner experiments. This would insure that the assumption these species are the major ones present in the ballistic situation is correct.

Further strand burner experimental data would be desirable, especially for nitramine propellants. The list of data necessary for modeling the DZ is mentioned earlier in this chapter. Experimentalists should strive to measure and report all the necessary data. The measurements of species concentrations should focus on majority species and N_2O, and should be as comprehensive as available techniques will allow. More studies of the dark-zone-length pressure dependence are needed.

Comprehensive 1-D propellant model studies could possibly be used to predict the DZ leading edge conditions. These could also be compared to the simplified DZ modeling results to test some of the assumptions in the latter.

Kinetics studies on elementary reactions which are desirable for DZ purposes are mentioned earlier in this chapter. Here one is reminded that studies on the more complex mixtures representative of the DZ are also needed. The range of interest for IB application is 1000 - 1800 K (possibly even as low as 500 K, depending on confirmation of recent preliminary ballistic simulator experiments at ARL), and pressure 5-40 atm. It would seem static and flow reactors are most likely to be able to reach the desired ranges. However, lower pressure (~1 atm) studies would also be useful since there is so little data available even for subsets of DZ mixtures at the lower temperatures. Because the DZ reactions are slow, such kinetics studies might be challenging. During such experiments, it seems checks of the reaction orders would be extremely desirable. It is, of course, recognized that inclusion of H_2O in the mixtures for kinetics experiments might be difficult. The study on the H_2/CO/NO mixture discussed earlier already has demonstrated the value of such test data. It would seem that studies on pairs of the mixtures' reactive components might be desirable as a first step towards comprehensive testing. For the nitramines, there is a worry that some key reaction may be missing from the current detailed mechanism. Since HCN and N_2O are key components present in nitramine DZs and not in nitrate esters, studies of HCN paired with NO, CO, CO_2 and, especially, N_2O seem most crucial.

3.8 References

1. a. D.E. Kooker, L.M. Chang, and S.L. Howard, "Flamespreading in Granular Solid Propellant. Influence of Propellant Composition", 32nd JANNAF Combustion Subcommittee Meeting, CPIA Publication 631, Vol. I, p. 397-408, 1995.

b. D.E. Kooker, S.L. Howard, and L.M. Chang, "Convective Ignition of a Granular Solid Propellant Bed: Influence of Propellant Composition", Twenty-Sixth Symposium (International) on Combustion, Naples, Italy, July-August 1996 (in press).

2. J.G. Sotter, "Chemical Kinetics of the Cordite Explosion Zone", Tenth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1965), p. 1405.

3. R.A. Fifer, A.J. Kotlar, M.S. Miller, and J.B. Morris, "Dark Zone Modeling for Delayed Ignition Kinetics", 27th JANNAF Combustion Subcommittee Meeting, CPIA Publication 557, Vol. I, p. 95, 1990.

4. J.A. Miller and C.T. Bowman, "Mechanism and Modeling of Nitrogen Chemistry in Combustion", Prog. Energy Combust. Sci., Vol. 15, p. 287, 1989.

5. J.A. Vanderhoff, W.R. Anderson, and A.J. Kotlar, "Dark Zone Modeling of Solid Propellant Flames", 29th JANNAF Combustion Subcommittee Meeting, CPIA Publication 593, Vol. II, p. 225, 1992.

6. W.R. Anderson, N. Ilincic, and K. Seshadri, "Studies of Reactions Pertaining to and Development of a Reduced Mechanism for the Double Base Propellant Dark Zone", 31st JANNAF Combustion Subcommittee Meeting, CPIA Publication 620, Vol. II, p. 387, 1994.

7. W.R. Anderson, N. Ilincic, N.E. Meagher, K. Seshadri, and J.A. Vanderhoff, "Detailed and Reduced Chemical Mechanisms for the Dark Zones of Double Base and Nitramine Propellants in the Intermediate Temperature Regime", 32nd JANNAF Combustion Subcommittee Meeting, CPIA Publication 638, Vol. I, p. 197, 1995.

8. N. Ilincic, W.R. Anderson, K. Seshadri, and N.E. Meagher, "Simplified Chemical Kinetic Mechanisms for Characterizing the Structure of the Dark Zones of Double Base and Nitramine Propellants", Twenty-Sixth Symposium (International) on Combustion, Naples, Italy, July-Aug, 1996 (in press).

9. W.R. Anderson, N. Ilincic, N.E. Meagher, K. Seshadri, and J.A. Vanderhoff, "Chemical Kinetic Mechanisms for Characterizing the Structure of the Dark Zones of Double Base and Nitramine Propellants", to be published.

10. A.E. Lutz, R.J. Kee, and J.A. Miller, "SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis", Sandia National Laboratories Report, SAND87-8248, October 1988.

11. W.R. Anderson, S.W. Haga, J.E. Nuzman, and A.J. Kotlar, to be published.

12. E.W. Diau, M.J. Halbgewachs, A.R. Smith, and M.C. Lin, "Thermal Reduction of NO by H_2: Kinetic Measurement and Computer Modeling of the HNO+NO Reaction", Int. J. Chem. Kinetics, Vol. 27, p. 867, 1995.

13. M. Rohrig and H.Gg. Wagner, "The Reactions of $NH(X^3\Sigma^-)$ with the Water Gas Components CO_2, H_2O, and H_2", Twenty-Fifth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1994), p. 975.

14. N. Ilincic, N.E. Meagher, K. Seshadri, and W.R. Anderson, to be published.

15. R.A. Fifer, private communication, unpublished.

4. COMBUSTION-MODEL DEVELOPMENT FOR INTERIOR-BALLISTIC APPLICATIONS

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This presentation was split into three parts. Section 4.1, "Solid-Propellant Flame-Zone Structure and Its Relationship to Interior-Ballistics Modeling," describes the flame structure which characterizes most solid gun propellants, how this structure is thought to influence ignition-delay phenomena in guns, and the current strategy at ARL for implementing finite-rate kinetics into interior-ballistic (IB) codes. Since part of this strategy involves the development of a first-principles combustion model, the rest of the presentation addressed a number of issues concerning some basic physical descriptions used in the current models. Section 4.2, "Evaporation-Mechanism Issues Arising from Frozen-Ozone Combustion Modeling," presents previously unrecognized physical aspects of the evaporation mechanism pertinent to both frozen ozone and RDX combustion, mostly having to do with modifications of the evaporation submodel required by the multicomponent nature of the liquid surface and by the approach to the thermodynamic critical point. Section 4.3, "Calculation of Multicomponent Interphase Phenomena," then summarizes the approach being taken at ARL to quantify these multicomponent and high-gas-density effects.

4.1 Solid-Propellant Flame-Zone Structure and Its Relationship to Interior-Ballistics Modeling

It is well known that almost all solid gun propellants (M30 is the sole exception) burn with a two-stage gas flame at pressures below about 5 MPa. The primary flame (i.e., that closest to the burning surface) is nonluminous and is sometimes termed the "fizz zone" in the older literature. At 1 MPa the reactions associated with the primary flame are completed within a few hundred micrometers of the surface for both nitramine and conventional nitrate-ester propellants. At the same pressure the leading edge of the secondary or luminous flame stands off from the surface by a few thousand micrometers, the intervening space frequently being referred to as the dark zone. One can compute that the reactions in the dark zone leading to the onset of the secondary flame take about 1 ms to occur for nitrate-ester propellants and about 6 ms for nitramine-composite propellants (at 1 MPa). Ignition delays observed for tank guns are in the 5-10 ms range for nitrate-ester propellants and can be significantly longer for nitramine-composite propellants. It has therefore been hypothesized that the relatively slow reactions associated with the induction of the secondary flame of nitramine-composite propellants are responsible for their correspondingly longer ballistic ignition delays. It is envisioned that the products of the primary flame, which are the reactants for the secondary flame, may become detached from their site of generation in the propelling-charge bed by the early convective cross flows arising from flame-spreading, but continue to react until their secondary flame energy is released at points in the

charge bed remote from the generation site. This hypothesis is consistent with high-speed cinematography of the flamespreading process in transparent gun simulators in which the igniter has been observed to function, the charge bed to go dark, then flame to erupt at the projectile end of the charge. It is this hypothesis which has motivated the detailed study of dark-zone kinetics at ARL. Recent IB calculations incorporating finite-rate kinetics for the secondary flame has confirmed the plausibility of this interpretation. (See section 2.)

At ARL a dual-track strategy has been adopted to characterize the finite-rate chemistry associated with secondary-flame induction. For near-term use in IB codes, the species concentrations and temperatures in the dark zone are being measured at several pressures, and these data can be used as the initial conditions for finite-rate chemistry calculations in IB codes. These reactants for the secondary flame are then presumed to be generated according to a measured burning rate. This approach should suffice for a first-order exploration of the coupling between dark-zone kinetics and ignition delays. The long-term strategy is to pursue development of a first-principles solid-propellant combustion model that will compute the regression rate and dark-zone temperature and species concentration for any pressure, initial temperature, and formulation.

Since the development of such a model is an ambitious undertaking, it is appropriate to summarize briefly the current state of the art. In the gas phase the transport phenomena at low densities are well understood and reliable computer codes are available for their solution. The high-density case, where binary collisions are less dominant, is more problematic and has not yet been treated by existing combustion models. Rate coefficients for gas-phase reactions (at low densities) are in relatively good shape, although cases of key reactions that are poorly known still arise. Progress is being made in the development of fundamental physical descriptions of the condensed-phase and inter-phase phenomena for cases where a melt layer premixes the reactants, but such descriptions are not yet complete. (See sections 4.1and 5.) Inroads are also starting to be made in the condensed-phase chemistry occurring during combustion, but much more work needs to be done in this area; this is probably the major unresolved difficulty. Finally, no attempts have yet been made to model (at a detailed-kinetics level) the three-dimensional inter-phase phenomena of a propellant that burns with degraded fragments of polymer backbone protruding from the surface (as has been observed for single- and double-base propellants) or a composite propellant whose burn rate is sensitive to oxidizer particle size.

4.2 Generalized Evaporation-Mechanism Issues Arising from Frozen-Ozone Combustion Modeling

At ARL the development of a first-principles, three-phase combustion model has first focused on the self-sustained combustion of frozen ozone.[1,2] This was done because the chemical simplicity of this system allowed concentration on the physical processes involved. Also, the frozen-ozone case is pertinent to RDX because, as with RDX, evaporation is the key surface-regression mechanism. Study of the frozen-ozone prototype revealed a number of implicit and untested assumptions which are common to all current detailed-kinetics models of RDX combustion. These assumptions are identified and discussed below.

1. Sticking coefficients have been assumed to be nonzero only for RDX vapor molecules. It is commonly (and justifiably) assumed that RDX vapor molecules reenter the liquid surface with unit sticking probability. However, there is no physical reason why all of the other gas-phase molecules at the surface should not also reenter the surface with unit probability as well. If this were allowed, then the composition of the surface liquid would be altered. This change in composition would in turn alter both the heat of vaporization absorbed by each molecule as it escapes the surface and its rate of escape, a matter of obvious importance to the energetics of the regression mechanism. (See section 4.3.) In addition, new chemical paths may open up in the condensed phase near the surface, or old paths may be changed as a result, and the altered mixture will affect the thermodynamic critical point for each escaping species. Since the species concentrations in the gas phase at the surface will also be changed, the chemistry associated with the heat feedback may also be affected. Finally, if species other than RDX are allowed to enter the liquid surface from the gas phase, it will be necessary to consider molecular diffusion in the liquid near the surface. Although diffusion rates in the liquid phase are normally small on the time scale of combustion, gas-phase species not present in the liquid except by virtue of surface absorption would, in the absence of diffusion, exhibit an infinite spatial gradient in the liquid at the surface. Since diffusion is a gradient-driven process, the surface density of these species, and therefore their rates of escape back into the gas phase, will necessarily depend on whether or not the diffusion process is modeled. The numerical significance of this effect is difficult to assess, short of actually doing the calculation.

2. The vapor pressure of RDX in current models has been assumed to be independent of pressure. Actually, as the molecular density in the gas phase at the surface increases due to pressure increases, the heat of vaporization decreases until at the critical point it is zero. The critical pressure of pure RDX is estimated to be 35-40 atm, so this phenomenon could affect the model-computed burning rate in the ballistically important low-pressure regime. The multicomponent nature of the surface liquid also affects the critical point for each species. To estimate the importance of this effect, we computed the burning rate of frozen ozone at its (pure-substance) critical pressure of 55 atm using an empirically derived pressure-dependent heat of vaporization. This resulted in a burning rate increase of 66% at the critical point.

3. The equilibrium vapor pressure of pure RDX has been used to compute the net evaporation rate and hence the regression rate. In reality, the vapor pressure of RDX will be affected by the presence of both condensed-phase decomposition products and the presence of absorbed gases. Both the heat of vaporization and the rate of vaporization are affected by the multicomponent nature of the surface.

4. The condensed-phase decomposition products have been assumed to be either dissolved completely in the liquid or to form bubbles instantaneously (depending on the model). Whether or not the products dissolve or form bubbles depends on whether the mixture-corrected vapor pressure of each species exceeds the total pressure. Again, the multicomponent nature of the surface is the controlling factor.

5. The net rates of desorption of condensed-phase molecules other than RDX have been assumed to be proportional to that of RDX. This assumption is an artifice to avoid

computing the rate of desorption of the condensed-phase product molecules directly. In reality these desorption rates follow their own mixture-corrected escape dynamics.

*6. **RDX combustion models to date have assumed the ideal gas law throughout the gas phase.*** Real-gas effects on the equation of state are known to be important above, say, 1000 atm at equilibrium flame temperatures. Gases near the surface, however, may be a factor of 4 or so colder than the flame temperature (and therefore more dense) so that the onset of real-gas effects near the surface may occur at only a few hundred atm. The transport coefficients under these conditions may also depart significantly from their low-density limits.

*7. **Equations of state and transport coefficients in the liquid have not yet been mixture corrected.*** This information is rarely known well even for the neat materials. Theoretical expressions for these quantities would be desirable.

4.3 Calculation of Multicomponent Interphase Phenomena

In this section the ARL approach to remedying the model shortcomings identified in section 4.2 is discussed. This approach is based on computing aggregate effects of superposed bimolecular intermolecular potential-energy functions. Work thus far has centered on use of the Lennard-Jones model potential. The generally good performance of the Lorenz-Berthelot rules for determining potential parameters for pairs of dissimilar molecules from the corresponding parameters of the pure-molecule parameters make this a particularly versatile choice for the multicomponent problem. However, it is recognized that the Lennard-Jones potential may not give the best results for polar molecules. For interactions between polar molecules and between polar and nonpolar molecules, the Stockmayer potential has proved useful for computing transport properties[3] and would be the logical candidate for extension of the approach. The intermolecular-potential approach itself has the advantage of being generalizable, in principle, to *ab initio* calculations of interaction potentials, though this option may involve an unacceptable computational burden. Even basing the treatment on standard model potentials has not yet been shown to be feasible for the case of multicomponent interphase phenomena, though it is now the routine means of computing gas-phase transport coefficients[3]. An alternative is to approach the problem through engineering correlations of properties and mixture properties, however, these methods are mostly empirical and may be difficult or impossible to apply to unstable intermediate species. In short, our opinion is that the model-potential approach, because of its theoretical underpinnings and greater potential generality, warrants an attempt at development before resorting to engineering correlations. A brief outline of our early efforts toward this end now follows.

Our starting point is to assume that a given molecule escaping from a multicomponent liquid surface interacts separately in a pairwise fashion with each of the molecules in the liquid. Estimates[4] of three-body interaction effects in molecular liquids suggest that the total interaction energy by this assumption may be in error by about 10%. A second assumption, which later will be modified, is that the molecules in the liquid phase may be treated as a continuum. As the test molecule is brought closer to the surface, the strong short-range repulsion predominates and

assures that molecules in the liquid will not come closer than some distance on the order of the Lennard-Jones collision diameter. One can visualize the path of the test molecule after it enters the liquid as tubular geometry, winding and twisting randomly at each collision with condensed-phase molecules. To account for this dynamic effect in a static potential, we further assume that the test molecule travels in a straight cylindrical tube of diameter on the order of the collision diameter and with zero potential inside the tube. Thus the molecule/surface potential has a sigmoidal shape with the test molecule moving in a region of constant potential when sufficiently deep in the liquid and with height of the potential hill equal to the internal energy change associated with evaporation. By virtue of the last two assumptions, one can integrate (analytically for the Lennard-Jones potential) over the pairwise interactions between the escaping molecule and all of the various molecules in the condensed phase to determine the molecule/surface potential.

One can also consider the additional effects of the interaction between the escaping molecule and all of the vapor-phase molecules. This can be accomplished analytically and leads to the very good approximation that the heat of vaporization of a pure material depends linearly on the difference between condensed-phase and gas-phase molecular density.

This simple theory can be further tested by computing the heats of vaporization of pure substances (for which L-J parameters are available) and comparing with experimental values. This was done for a collection of about 60 molecules (about equally divided between nonpolar and polar types) with the encouraging result that heats of vaporization could be predicted within a standard deviation of 16% with no adjustable constants. This accuracy could be improved to about 12% by empirically parameterizing the tube radius and L-J well depth. Monte-Carlo simulations are being planned to guide this model-building effort further.

The molecule/surface potential energy function gives the heat of desorption immediately, being simply related to the height of the potential hill. One is also interested in computing the rate of evaporation of a molecule from the multicomponent liquid surface. For this task one needs a kinetic theory of evaporation. If one considers the escaping molecule as being trapped in in the condensed phase at the foot of this potential hill, the flux of escaping molecules can be computed from kinetic theory as one fourth the product of the condensed-phase number density times the average velocity exceeding that required to overcome the potential barrier. This average escape velocity is of course related to the Boltzman factor at the surface temperature. Using this theory one can then predict vapor pressures for pure substances and compare with experimental values. This was done at the normal boiling point for the same set of about 60 molecules, resulting in a prediction of the vapor pressure with a standard deviation of about 50%. Empirical parameterizations lowered this error to about 30%. Thus, in spite of the simplicity of these physical models, encouraging results have been achieved. Work continues to refine the model assumptions based on insights which will be gained from molecular dynamic simulations of the evaporation process using the same model potentials. It is hoped that, through these model potentials, a degree of universality similar to that now routinely used for the calculation of gas-phase transport coefficients may emerge.

4.4 Summary

A number of studies have led to the conclusion that finite-rate chemistry can have an important influence on the flamespreading phase of the interior ballistics of guns. We have outlined here the strategy developed at ARL for determining quantitative descriptions of these kinetics for use in IB codes. The strategy involves providing approximate models for near-term concept exploration in IB codes and pursuing the longer term approach of developing a first-principles theory of propellant combustion. The current state of the art in fundamental models targets the combustion of pure RDX, a crystalline component of XM39 and M43 gun propellants. This presentation has identified and discussed a number of implicit, nonrigorous assumptions in the current RDX-combustion models, mostly pertaining to the effects of the multicomponent nature of the surface melt layer on the regression mechanism and high-density effects. The ARL research approach to characterizing these phenomena in terms of fundamental molecular interactions was outlined. Other phenomena, such as condensed-phase reactions and high-density transport coefficients, important to a fundamental description of propellant combustion, are as yet in a primitive state of understanding, though advances in theoretical chemistry, notably in the density-functional theory, coupled with molecular dynamics, give realistic promise to having practical theoretical descriptions available in the near future.

In view of the current uncertainties associated with several of the subprocesses of energetic-material combustion and the emerging nature of an adequate theoretical framework to describe them, it is our opinion that the goal of modeling the combustion of real propellants will be most expeditiously achieved through the stepwise consideration of a well chosen sequence of progressively more complex energetic substances. The ozone prototype has proved its heuristic value in identifying previously unrecognized physical effects as described above. No doubt other intermediate-complexity prototypes such as hydrazine, ethyl nitrate, or nitroglycerine will prove to be similarly useful in the approach to modeling multicomponent propellants.

4.5 References

1. Martin S. Miller, "Development of a 3-Phase, Detailed-Kinetics, Steady-State Combustion Model with Heterogeneous Reaction: Application to Frozen Ozone," 32nd JANNAF Combustion Meeting, Huntsville, AL, 23-27 October 1995.

2. Martin S. Miller, "Three-Phase Combustion Modeling: Frozen Ozone, A Prototype System," Invited Paper, Materials Research Society Symposium Proceedings Volume 418, Materials Research Society, Pittsburgh, PA, 1996.

3. R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, and J. A. Miller, "A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties," Sandia National Laboratories Report SAND86-8246, 1988.

4. P. Aloysius Monson, Maurice Rigby, and Wiliam A. Steele, "Non-Additive Energy Effects in Molecular Liquids," Molecular Physics, Vol. 49, pp. 893-898, 1983.

5. RECENT ADVANCES IN MODELING OF RDX PROPELLANT IGNITION AND COMBUSTION

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The purpose of this presentation is to provide an overview of recent advances in modeling of nitramine-propellant combustion and ignition, with emphasis placed on the research accomplishments, difficulties, and needs. It contains the following three sections.

1. Combustion of RDX Monopropellant
2. Ignition of RDX Monopropellant
3. Research Needs

Most of the results presented herein were obtained under a University Research Initiative (URI) program sponsored by the Army Research Office. A synopsis of the presentation material is given below.

5.1. Combustion of RDX Monopropellant

5.1.1. Background

Cyclo-trimethylene-trinitramine (or hexahydro-1,3,5-trinitro-1,3,5-triazine) is an energetic compound which has been widely used in gun propellants, producing high specific impulse but little smoke, toxicity, and corrosion. This compound is given the acronym RDX since it was named "Royal Daughter's Explosive" by British chemists. In spite of its broad applications, fundamental understanding of the detailed physico-chemical processes involved in the combustion of RDX monopropellant remains limited. The major obstacle lies in the difficulties in conducting experimental and theoretical investigations into the combustion-wave structures at scales sufficient to resolve the detailed chemical kinetic pathways and thermodynamic processes in the subsurface two-phase region, as well as in the gas phase. Comprehensive reviews of works conducted prior to 1984 are given by Boggs[1] and Fifer,[2] and the state of the understanding up to 1990 is summarized by Alexander et al.[3]

Research on RDX and related nitramine-propellant combustion can be roughly categorized into three areas: (1) treatment of condensed-phase thermal-decomposition mechanisms and phase transition, (2) decomposition and gas-phase reaction kinetics, and (3) modeling of overall combustion wave structures. Attempts to elucidate the thermal-decomposition mechanisms of RDX have been made during the past four decades, providing useful information about the initial chemical pathways and global reaction rates of the processes, $RDX \rightarrow products$. Brill et al.[4] conducted a comprehensive review of this subject with emphasis placed on determination of the rate constants written in the Arrhenius form: $k=A\cdot\exp(-E_a/R_uT)$. More than 21 sets of data

acquired during the period from 1949 to 1988 were compiled, covering a temperature range of 316-540 K in all three thermodynamic phases of solid, liquid, and gas.

Unlike research on thermal decomposition, only a few studies have been devoted to RDX gas-phase flame structures. Korobeinichev et al.[5] measured species-concentration profiles at 0.5 atm using a combined microprobe sampling and time-of-flight mass spectrometry (TOFMS) technique. The propellant sample was ignited by a hot wire and achieved self-sustained combustion without further heat addition. Measurements were performed only for the gas-phase region with a resolution (better than 100 μm) sufficient to resolve flame structures at low pressures, but not fine enough to analyze the surface-reaction zone. The microprobe mass spectroscopy technique was later extended by Litzinger and co-workers[6,7] to include a triple-quadrupole mass spectrometer (TQMS) capable of differentiating and quantifying species which could contribute to the same mass, such as N_2 and CO to mass 28 and N_2O and CO_2 to mass 44. The experiments were conducted in an argon environment over a pressure range of 0.1 to 3 atm, and a CO_2 laser was used to initiate and sustain combustion of the test samples at several heat fluxes ranging from 50 to 600 W/cm^2. Hanson-Parr and Parr[8] conducted pioneering measurements of temperature and species concentration profiles of RDX flames using nonintrusive planar laser-induced fluorescence (PLIF) and UV-visible absorption techniques. The samples were burnt in air at 1 atm under a CO_2 laser heat flux of 600 W/cm^2. The reported temperature profile, obtained by assembling thermocouple measurements and rotational and vibrational UV/visible absorption spectra of NO and OH, revealed the presence of a dark zone with a temperature plateau around 1700 K. Recently, Zenin[9] conducted experimental investigations into self-deflagrating RDX flames, using a micro-thermocouple (MTC) technique covering a pressure range from 1 to 90 atm.

In regard to theoretical modeling, most of the early studies employed global reaction schemes for gas-phase processes.[10] Almost no information was given about detailed chemical pathways and transport mechanisms. The first development of a comprehensive model was performed by Ermolin et al.[11] in an effort to simulate experimentally measured species-concentration profiles. The model included 23 species and 49 reactions in the gas phase, but required that the propellant surface conditions be explicitly input in order to match the experimental data. A substantial improvement was made by Melius[12] to relax this constraint. His formulation simultaneously took into account the thermal decomposition of RDX and the ensuing chemical reactions to an extent that the key heat-release mechanisms could be identified. The thermochemical properties of large molecules and related kinetic data were estimated using a quantum chemical method based on the bond-additivity corrected Møller-Plesset 4th-order perturbation (BAC-MP4) scheme. Recently, Yetter et al.[13] refined Melius' reaction mechanism to include the submodels of reactions among the major intermediate products such as CH_2O, NO_2, N_2O, H_2, HCN, and NO. The kinetic parameters were also updated through flow-reactor experiments spanning temperatures from 550 to 1200 K and pressures from 1 to 20 atm, respectively, with residence times between 10 and 2000 ms.

5.1.2. Current Status

The most comprehensive analysis of RDX monopropellant combustion to date was conducted by Yang and coworkers at Penn State,[14] under the sponsorship of ARO. The model accommodates detailed chemical kinetics and transport phenomena in the gas phase, as well as thermal decomposition and subsequent reactions in the condensed phase. The formation of gas bubbles in the molten surface layer due to molecular degradation and thermodynamic phase transition is also included to provide a complete description of the observed physical phenomena. The model is capable of treating the entire combustion-wave structure, with the instantaneous burning rate calculated as part of the solution. Various important aspects of RDX burning characteristics are examined over a broad range of pressures, with special attention given to the effect of subsurface two-phase flow on propellant deflagration.

To facilitate the analysis, the entire combustion-wave structure is conveniently segmented into three regions: an inert solid-phase region, a chemically active near-surface two-phase layer, and a gas-phase region. During burning, the propellant remains inert in the solid phase until the temperature reaches the melting point, at which thermodynamic phase transition occurs. Molecular degradation and evaporation of RDX then take place in the resulting liquid, generating bubbles and forming a two-phase layer. The propellant subsequently undergoes rapid evaporation and decomposition in the near field immediately above the foam layer. Oxidation reactions continue to occur, releasing an enormous amount of energy in the gas phase, with the final temperature reaching the adiabatic flame temperature. A brief summary of the theoretical formulation of physico-chemical processes in the various regions is given below. Detailed derivations of the described problem can be found in Liau and Yang [14].

5.1.2.1. Gas-Phase Processes

The analysis for the gas phase is based on mass, energy, and species transport for a multicomponent chemically reacting system containing N species, and it accommodates finite-rate chemical kinetics and variable thermophysical properties.

The reaction mechanisms proposed by Melius[12] and Yetter et al.[13] are employed to model the gas-phase chemical kinetics. Melius' scheme consists of 38 species and 158 reactions, being derived by extending a generalized hydrocarbon/air flame model of Miller and co-workers.[15-17] The mechanisms include the oxidation of HCN, the conversion of NH_i species to NO and N_2, and the flame chemistry of C_2N_2/NO_2. Additional reactions are considered to treat the decomposition of RDX and the subsequent reactions among intermediate species. The thermochemical data for species not in the literature were calculated using the BAC-MP4 quantum chemical method. Yetter et al.[13] adopted the same initial decomposition scheme for RDX propellant as that proposed by Melius, but used a modified set of subsequent reactions. Their model is based on a hierarchical approach for collecting kinetic data and the specific chemical submodels that are required to form the gas-phase combustion mechanism. In particular, three kinetic submodels of increasing complexity (N_2O decomposition, H_2/NO_2 reaction, and CH_4/N_2O reaction) are established using the results from kinetic experiments over a broad range of temperature and pressure. Although the trends of the Melius and Yetter models are consistent in terms of

predicted temperature and species concentration profiles, significant differences are observed in many of the pathways of secondary reactants.

5.1.2.2. Subsurface Processes

The foam layer contains both a liquid region and gas bubbles. Below the foam layer is an inert solid-phase region, which undergoes essentially no chemical reactions. The foam layer and solid-phase region are referred to as the subsurface region. The physico-chemical processes that occur in the foam layer are extremely complex, involving an array of intricacies such as thermal decomposition, bubble nucleation and subsequent growth, liquid-phase and gas-phase reactions, interfacial transport of mass and energy between liquid and gas phases, etc. A two-phase model based on a spatial averaging technique is employed to formulate these complicated phenomena. The analysis utilizes an integral form of the conservation equations for control volumes occupied separately by gas and liquid phases.

5.1.2.3. Subsurface Chemical Kinetics and Phase Transition

Thermal decomposition and its ensuing reactions in the foam layer have been investigated by many researchers, as summarized in Liau and Yang [14]. Since these processes are extremely complicated and contain many uncertainties, a thorough consideration of all physico-chemical mechanisms involved does not appear feasible. A global thermal decomposition model of Brill et al.,[18] which is derived from a well-calibrated temperature-jump/Fourier transform infrared (T-jump/FTIR) spectroscopy experiment,[19] is therefore adopted here. This model is a viable alternative, providing reasonably accurate information concerning the major chemical pathways. The scheme first assumes two degradation reactions in the condensed phase,

$$RDX_{(c)} \xrightarrow{k_1} 3CH_2O + 3N_2O \qquad \text{(R1)}$$

$$RDX_{(c)} \xrightarrow{k_2} 3HCN + \frac{3}{2}NO + \frac{3}{2}NO_2 + \frac{3}{2}H_2O \qquad \text{(R2)}$$

Reaction R1 is exothermic and is favored at low temperatures. The second reaction, R2, initiated by N-NO_2 bond cleavage, is endothermic and prevails at high temperatures. The net amount of heat released from (R1) and (R2) is experimentally observed to be small.[18] Subsequent reactions among the products of (R1) and (R2) may occur and provide the thermal energy required to sustain pyrolysis. Brill[20] examined several plausible secondary reactions (such as CH_2O+NO_2, CH_2O+N_2O, and HCN+NO_2) and their corresponding reaction rates. Results from rapid thermolysis of RDX[18] indicate that the following reaction,

$$NO_2 + CH_2O \xrightarrow{k_3} NO + CO + H_2O \qquad \text{(R3)}$$

is probably the most important secondary reaction in the condensed-phase environment. It appears, however, that its reaction rate is too low to play a significant role within the foam layer.

In addition to the thermal decomposition and subsequent reactions (R1)-(R3), thermodynamic phase transition from liquid to vapor RDX is required to provide a complete description of the mass conversion process.

$$RDX_{(c)} \Leftrightarrow RDX_{(g)} \qquad \text{(R4)}$$

The process consists of both evaporation and condensation, and it can be modeled using gas-kinetic theory.

5.1.3. Summary of Representative Results

A series of calculations was carried out to study the RDX combustion behavior over a broad range of pressures and initial temperatures. Various important burning characteristics were investigated systematically, with emphasis placed on the detailed flame structure and the effect of the subsurface two-phase layer on propellant deflagration. Good agreement between the experimental and predicted burning rates was achieved as shown in Figure 1. This is to be expected, however, since no slope breaks or other anomalies were revealed experimentally in the measured burning rate. Similarly, the predicted temperature and pressure sensitivities also agreed quite well with those deduced from experiments.

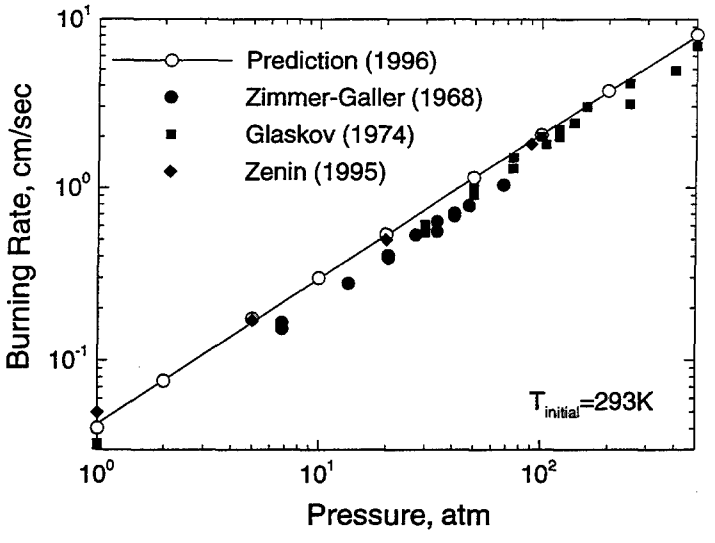

Figure 1: Effect of pressure on measured and predicted burning rates.

The temperature distribution in the gas phase indicates a monotonic increase from the surface to the end of the flame zone. This monotonic temperature increase in the gas and condensed phases is shown in Figure 2 for four different pressures. It should be noted that the final flame temperatures are established within a distance of 1 mm or less, revealing the difficulty of probing such flames using either intrusive or nonintrusive diagnostic techniques. It is evident that experimental approaches for stretching these flames at reduced pressures should be pursued

in order to provide additional data for model validation. No evidence was found of a temperature plateau near the surface suggestive of a dark zone.

The calculated species-concentration profiles suggest a multistage reaction mechanism in the gas phase. Presently, validation of the chemical kinetics model is performed by comparing the predicted evolution of major species with those obtained from measurements, as shown in Figure 3. The agreement appears to be reasonable for all species except N_2. It is evident that validation of the reaction mechanism, which suggests the presence of several reaction zones within the flame, cannot be performed by comparing the results of major species alone. Although there is encouraging consistency between the present predictions with available experimental data of self-sustained RDX combustion, further investigations are needed to establish a more complete understanding of the flame structure under a broad range of ambient conditions.

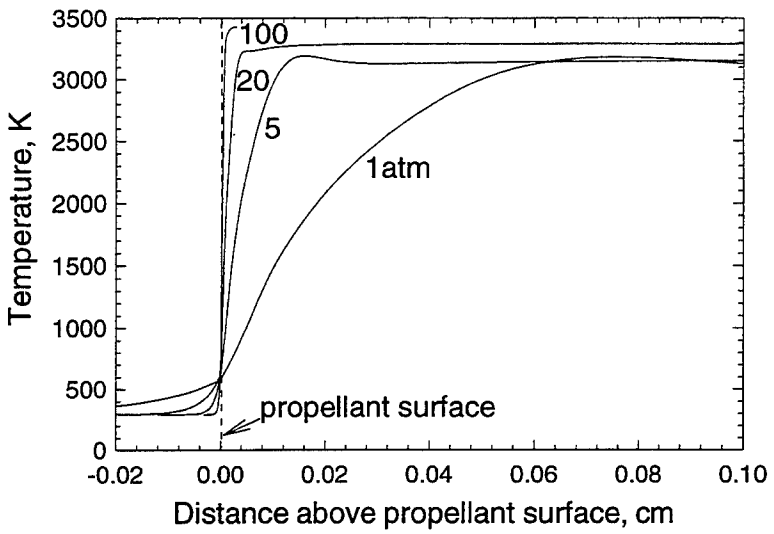

Figure 2: Effect of pressure on temperature profile within gas and condensed phases.

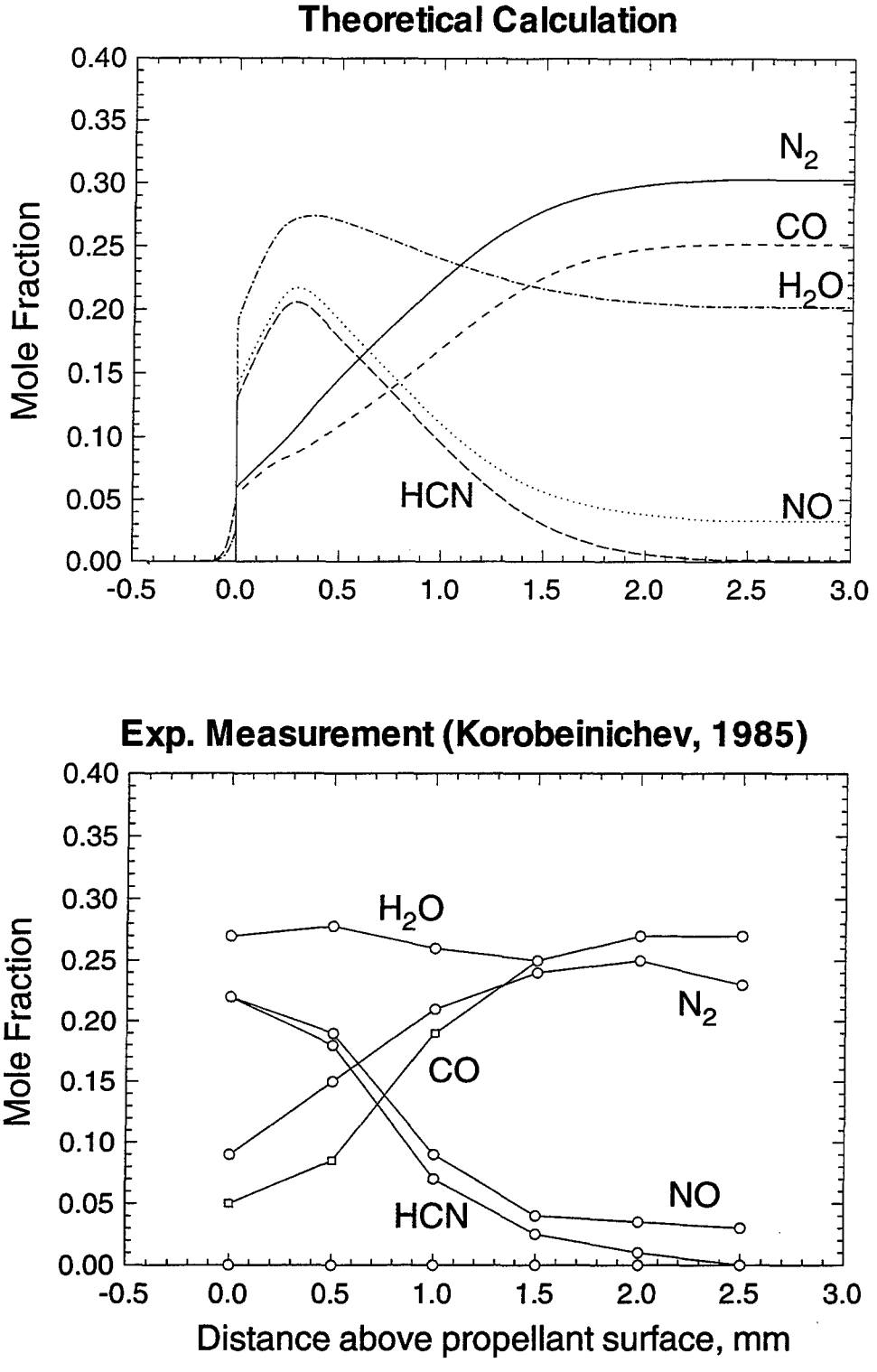

Figure 3: Predicted and measured major species at pressure of 0.5 atm.

5.2. Ignition of RDX Monopropellant

5.2.1. Background

Transient burning behavior, such as ignition and extinction of solid propellants, involves an array of complexities. A comprehensive discussion of this subject is given in Price et al.[21] and Hermance.[22] Russian scientists also conducted detailed investigations, and the state of the understanding up to 1989 was summarized by Vilyunov and Zarko.[23]

Existing models of solid-propellant ignition can be classified into three categories: (1) solid-phase reaction models (or reactive-solid models), (2) heterogeneous reaction models, and (3) gas-phase reaction models. Solid-phase reaction models treat exothermic reactions in solids. Linan and Williams[24,25] conducted analyses of reactive solids exposed to radiative heat flux by means of an asymptotic method based on activation energies. Analytical relations among dimensionless heat release, activation energy, and ignition delay were obtained. Baer and Ryan[26] and Bradley[27] conducted numerical analyses with similar approaches and obtained better agreement with experimental data on the pressure dependence of ignition delay.

Heterogeneous reaction models consider the propellant surface as a fuel source subjected to heterogeneous reactions, with oxidizer supplied by the external gas-phase environment. Williams[28] developed an analysis using the Laplace transform method and observed two interesting phenomena. The first was a continual, slow rise in surface temperature to some final temperature, while the second was a slow rise in surface temperature for a sustained period of time, followed very quickly by a sharp increase in surface temperature. Several heterogeneous reaction models[29-34] were subsequently developed, providing explicit expressions for ignition delay in terms of chemical parameters of the underlying reactions.

Gas-phase reaction models[35-39] state that ignition occurs in the gas phase due to exothermic reactions between the gaseous fuel and oxidizer. The propellant first decomposes and releases gaseous fuel and oxidizer due to an external heat source and/or heat feedback from gas-phase exothermic reactions. As the gaseous reactants build up, a self-accelerating chemical mechanism may form, causing a rapid rise in the temperature. The models provide more information (not only on ignition delay but also on temperature and species concentration profiles) and are applicable to various ignition problems.

5.2.2. Current Status

In spite of the progress made so far toward simulating of the ignition processes of solid propellants, most of the existing models consider only global reactions and offer limited knowledge about detailed chemical pathways and transport processes. Furthermore, the initial gasification rate of the propellant under the influence of an external stimulus is either treated as an empirical parameter or modeled using a simple Arrhenius law for surface pyrolysis. No account is made of subsurface reactions and the coupling between gas and condensed phases.

Information about the onset of flame development, time evolution of temperature and species-concentration profiles, and transition to steady-state combustion remains largely unknown.

The purpose of the present work is to develop a time-accurate analysis capable of treating the processes of RDX monopropellant ignition.[40] The formulation extends the steady-state combustion model[14] to accommodate the temporal evolution of physico-chemical processes in various parts of the combustion wave. The analysis is based on the conservation equations of mass, momentum, energy, and species concentration, with special attention given to the dynamic coupling between the gas- and condensed-phase processes. The chemical kinetics scheme follows the one employed in the steady-state analysis, involving 45 species and 232 reactions in the gas phase and two decomposition pathways in the condensed phase. Vaporization and condensation are also included within the foam layer and at the interface between the foam layer and the gas-phase region to provide a complete description. The model is capable of treating the entire history of an ignition event. Included as part of the solution are propellant surface temperature and instantaneous burning rate.

The analysis has been applied to study laser-induced ignition of RDX monopropellant under a variety of CO_2-laser heat fluxes and ambient pressures. Results have shown good agreement with measured ignition-delay times based on the appearance of a CN flame. The conversion of NO and HCN to N_2, CO, and H_2O is identified as the key exothermic process in achieving ignition. Overall trends in flame development, such as the occurrence of ignition kernel and time evolution of flame-standoff distance, are quantitatively consistent with experimental observations. However, the model requires further refinements in order to more accurately predict the entire ignition event, in particular the initial standoff distance of the CN flame.

To illustrate the complex evolution of the gas-phase temperature during laser-initiated combustion, Figure 4 is shown. The RDX monopropellant is subjected to a constant laser heat flux of 400 W/cm^2, and the evolved gases undergo a radial expansion above the surface according to the area ratio $A_{max}/A_0 = 5$. In Figure 4, the temperature profile is shown at eleven different instances of time. For times $t \leq 1$ ms, processes are dominated by heat conduction into both the solid and gas phases. That is, no phase transition or chemical reactions occur at any significant

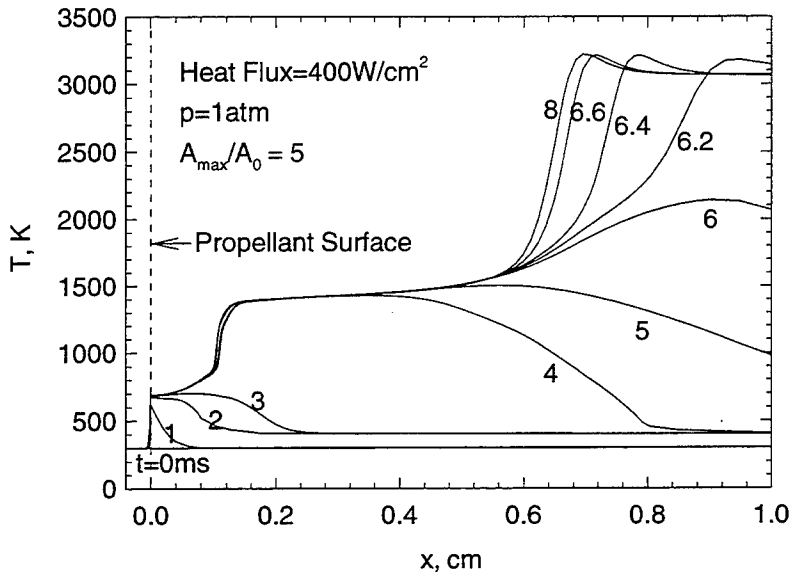

Figure 4: Evolution of gas-phase temperature during ignition of RDX.

rate due to the low surface temperatures. For $1 < t < 3$ ms, evaporation and decomposition of RDX take place, causing the initially present gas-phase species Ar to be displaced from the surface. However, the temperatures are too low to cause significant heat release from reactions among the decomposition products. For $3 < t < 5$ ms, reactions typical to those taking place in the primary reaction zone, namely between CH_2O and NO_2 species, are now significant. The predicted temperature profile is similar to the one observed in the dark zone of nitramine-composite propellants during steady-state combustion. Over this time interval, an accumulation of reactive dark-zone species occurs, as well as an increase in the corresponding temperature profile is noticed. For $t > 5$ ms, species present in the dark zone ($T \approx 1500$ K) are converted into final products, causing a rapid rise in the gas-phase temperature. Near $t = 8$ ms, the ignition of the RDX monopropellant is established. From a computational viewpoint, one should note the complexity that is involved with formulating a sophisticated, adaptive numerical scheme capable of capturing the various time scales associated with the temperature profile alone. Additional ones are introduced as a result of chemical reactions. Hence, the computational effort is significant.

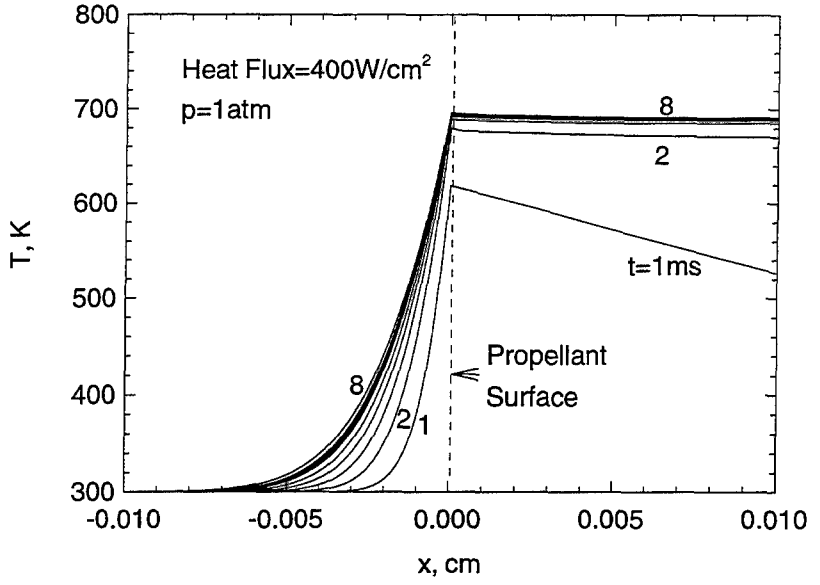

Figure 5: Evolution of the condensed-phase and near-surface temperatures during ignition of RDX.

The corresponding evolution of temperatures within the condensed-phase and near-surface region are illustrated in Figure 5. The results suggest the following. First, the temperature profile within the condensed phase is typical to one involving heat conduction. The thermal penetration depth is about 75 μm at the time of ignition. Second, the effect of the transition from a dark-zone temperature profile ($3 < t < 5$ ms) to ignition ($t > 8$ ms) on the condensed-phase temperature profile is minimal. This is also to be expected from an examination of Figure 4. Finally, since the near-surface temperature profile is very flat, evaporation of RDX is clearly the dominant process of converting condensed-phase species into gas-phase species. In addition, one should note the complexity and the thinness of the temperature profiles within both the condensed and gas phases. Hence, it will be a challenging task to capture these rapidly varying temperature profiles using either intrusive or nonintrusive diagnostic techniques in order to validate the existing model of laser-induced ignition of RDX monopropellant.

5.3. Research Needs

In spite of the substantial progress made so far in the modeling of RDX monopropellant combustion and ignition, further work is undoubtedly needed. To enhance our understanding of this complex phenomenon, research in several areas is identified.

5.3.1. Gas-Phase Chemical Kinetics

The chemical kinetics model developed by Melius (and later refined by Yetter) provides a reasonable description of the chemical pathways of RDX combustion. However, there still remains quite a few uncertainties regarding the initial decomposition process. As a result, the

present model slightly overpredicts the location of the ignition kernel under the influence of CO_2-laser heat flux. The effect of pressure on chemical kinetics should also be studied for gun interior ballistic applications.

5.3.2. Subsurface Reactions

Subsurface reactions are intimately related to initial decomposition pathways, and thus play a decisive role in determining propellant surface conditions and burning behavior. The current model is based on a phenomenological description which is deduced from a model of the T-jump experiment and FTIR absorption data.[19] It involves two global decomposition reactions and one heat release reaction in the condensed phase. Further studies of this matter, especially under higher heating rates and ambient pressures, are required to provide detailed information commensurate with the comprehensive gas-phase chemical kinetics model.

5.3.3 Diagnostics for Model Validation

It is evident that the existing one-dimensional model of RDX ignition and steady-state combustion has reached a level of sophistication that warrants a thorough validation from a wide range of experimental data. However, by using the model to conduct a sensitivity analysis, the experimentalists should be provided with priority items for investigations and data acquisition. At this time, it is apparently evident that detailed and accurate experimental data are needed in the following areas: (1) temperature and species profiles during laser-assisted ignition and combustion showing the presence of a two-stage flame structure and stretched primary reaction zone, (2) thermal decomposition and associated kinetic rates of large molecules in the near-surface region of the gas phase, (3) temperature and species profiles within the liquid phase as well as the associated kinetic rates, (4) interfacial mass transfer rates between the liquid and gas phases in both single- and multicomponent systems, (5) thermodynamic property data including, among others, surface tension, viscosity, specific heats, thermal conductivity, heat of formation, and radiative properties of the liquid and gas phases, and (6) identification of sites of nucleation, rates and size of bubble growth, bubble size distribution, and thickness of the foam layer. Furthermore, it is necessary that the experimental data are verified by comparing the results from different diagnostic techniques covering the same test condition, such as intrusive (mass spectroscopy) versus nonintrusive (UV-visible/FTIR/mid-IR/Raman absorption) methods. In addition, to limit the scope and simplify the conduct of such experiments, it is suggested that studies are limited to near-atmospheric pressures.

5.3.4 Consideration of Binder Ingredients

To acquire a deep understanding of the ignition and combustion behavior of a real solid propellant, the physicochemical processes of each constituent ingredient must first be studied and thoroughly understood. Since our understanding of the ignition and combustion behavior of RDX is maturing, attempts should be made to study the ignition and combustion behavior of a pseudo-propellant comprising well-defined ingredients. It is evident that one should consider only a single binder ingredient with RDX monopropellant for the purpose of keeping the system

under study as simple as possible. Efforts are underway to study the interactions between RDX and cellulose acetate butyrate (CAB), since the thermal decomposition characteristics of CAB alone have been elucidated.[41] In addition to forming a sooty residue, the decomposition products and pathways of this molecule appear to be quite complex. CAB is one of the primary binder ingredients in the XM39 propellant, which contains 76% RDX, 12% CAB, 7.6% acetyl triethyl acetate (ATEC), and 4% nitrocellulose (NC) by weight. Experiments conducted at Penn State have revealed that pressed mixtures of RDX and CAB do not establish a visual two-stage flame structure and the adiabatic flame temperature is established in close vicinity of the burning surface. Hence, probing of the flame zone using either intrusive or nonintrusive techniques may be quite difficult. However, a two-stage flame structure is observed and measured for the XM39 propellant.[42] To study a propellant which possesses an intellectually interesting and experimentally challenging two-stage flame structure, it may be useful to consider other polymeric binder ingredients, whose molecular structures and thermal decomposition characteristics are simpler than those of either CAB, ATEC or nitrocellulose.

5.3.5. High-Pressure Phenomena

High-Pressure Thermodynamics: Most gun propellants ignite and burn at ambient pressures and temperatures well above the thermodynamic critical points of the constituent ingredients. Under this condition, the propellant surface may undergo a thermodynamic phase transition from its subcritical to supercritical state. The enthalpy of vaporization and surface tension reduce to zero, and the effect of interfacial thermodynamics vanishes. The entire field becomes continuous, with no abrupt variations of thermophysical properties observed across the interface. This phenomenon must be carefully investigated since the propellant near-surface behavior may become qualitatively different from that at low pressures.

High-Pressure Transport Phenomena: It is well established that fluid transport properties change drastically in the transcritical stage, a phenomenon commonly known as near-critical enhancement. This phenomenon is particularly important in the near-surface region due to the relatively low-temperature but high-pressure conditions. All the existing models of propellant combustion ignore the transcritical transport anomaly that prevails during thermodynamic phase transition at high pressures. The effects of pressure on transport and thermodynamic properties are practically ignored.

High-Pressure Fluid Dynamics: The molten surface layer present on most burning solid propellants may become highly non-Newtonian due to their heavy molecular structures. The constitutive laws for shear stress, thermal diffusion, and mass transfer may deviate substantially from those developed for Newtonian fluids. This problem deserves careful investigation, including property data on surface tension and viscosity.

5.4. References

1. Boggs, T.L., "The Thermal Behavior of Cyclotrimethylene-trinitramine (RDX) and Cyclotetramethylene-tetranitramine (HMX)," *Fundamentals of Solid Propellant*

Combustion, AIAA Progress in Astronautics and Aeronautics Series, Edited by Kuo, K.K. and Summerfield, M., Vol. 90, 1984, pp. 121-175.

2. Fifer, R.A., "Chemistry of Nitrate Ester and Nitramine Propellants," *Fundamentals of Solid Propellant Combustion*, AIAA Progress in Astronautics and Aeronautics Series, Edited by Kuo, K.K. and Summerfield, M., Vol. 90, 1984, pp. 177-237.
3. Alexander, M.H., Dagdigian, P.J., Jacox, M.E., Kolb, C.E., Melius, C.F., Rabitz, H., Smooke, M.D., and Tsang, W., "Nitramine Propellant Ignition and Combustion Research," *Progress in Energy and Combustion Science*, Vol. 17, 1991, pp. 263-296.
4. Brill, T.B., Gongwer, P.E., and Williams, G.K., "Thermal Decomposition of Energetic Materials 66. The Kinetic Compensation Effect in HMX, RDX, and NTO," *Journal of Physical Chemistry*, Vol. 98, Issue No. 47, November 24, 1994, pp. 12242-12247.
5. Korobeinichev, O.P., Kuibida, L.V., Orlov, V.N., Tereshchenko, A.G., Kutsenogii, K.P., Mavliev, R.V., Ermolin, N.E., Fomin, V.M., and Emel'yanov, I.D., "Mass Spectrometric Probe Study of the Flame Structure and Kinetics of Chemical Reactions in Flames," *Mass-Spektrom. Khim. Kinet.*, 1985, pp. 73-93.
6. Fetherolf, B.L. and Litzinger, T.A., "Chemical Structure of the Gas-Phase Above Deflagrating RDX: Comparison of Experimental Measurements and Model Predictions," *Proceedings of 30th JANNAF Combustion Subcommittee Meeting*, CPIA Publication No. 606, Vol. II, 1993.
7. Litzinger, T.A., Fetherolf, B.L., Lee, Y.-J., and Tang, C.-J., "A Study of the Gas-Phase Chemistry of RDX: Experiments and Modeling," *Journal of Propulsion and Power*, Vol. 11, No. 4, July-August 1995, pp. 698-703.
8. Hanson-Parr, D. and Parr, T., "RDX Flame Structure," *Proceedings of Twenty-Fifth Symposium (International) on Combustion*, The Combustion Institute, 1994, pp. 1635-1643.
9. Zenin, A., "HMX and RDX: Combustion Mechanism and Influence on Modern Double-Base Propellant Combustion," *Journal of Propulsion and Power*, Vol. 11, No. 4, July-August 1995, pp. 752-758.
10. BenReuven, M., Caveny, L.H., Vichnevetsky, R.J., and Summerfield, M., "Flame Zone and Sub-Surface Reaction Model for Deflagrating RDX," *Proceedings of Sixteenth Symposium (International) on Combustion*, The Combustion Institute, 1976, pp. 1223-1233.
11. Ermolin, N.E., Korobeinichev, O.P., Kuibida, L.V., and Formin, V.M., "Study of the Kinetics and Mechanism of Hexogen Flames," *Fizika Goreniya I Vzryva*, Vol. 22, No. 5, 1986, pp. 54-64.
12. Melius, C.F., "Thermochemical Modeling: I & II.," *Chemistry and Physics of Energetic Materials*, Edited by Bulusu, S. N., Kluwer Academic Publication, Inc., 1990, pp. 21-78.
13. Yetter, R.A., Dryer, F.L., Allen, M.T., and Gatto, J.L., "On the Development of Gas-Phase Reaction Mechanisms for Nitramine Combustion," *Journal of Propulsion and Power*, Vol. 11, No. 4, July-August 1995, pp. 683-697.
14. Liau, Y.-C. and Yang, V., "Analysis of RDX Monopropellant Combustion with Two-Phase Subsurface Reactions," *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp.729-739.
15. Glarborg, P., Miller, J.A., and Kee, R.J., "Kinetic Modeling and Sensitivity Analysis of Nitrogen Oxide Formation in Well-Stirred Reactors," *Combustion and Flame*, Vol. 65, 1986, pp. 177-202.

16. Miller, J.A., Branch, M.C., McLean, W.J., Chandler, D.W., Smooke, M.D., and Kee, R.J., "The Conversion of HCN to NO and N_2 in H_2-O_2-HCN-Ar Flame at Low Pressure," *Proceedings of Twentieth Symposium (International) on Combustion*, The Combustion Institute, 1984, pp. 673-684.
17. Thorne, L.R., Branch, M.C., Chandler, D.W., Kee, R.J., and Miller, J.A., "Hydrocarbon-Nitric Oxide Interactions in Low-Pressure Flames," *Proceedings of Twenty-first Symposium (International) on Combustion*, The Combustion Institute, 1986, pp. 965-977.
18. Brill, T.B., Brush, D.G., Patil, D.G., and Chen, J.K., "Chemical Pathways at a Burning Surface," *Proceedings of Twenty-Fourth Symposium (International) on Combustion*, The Combustion Institute, 1992, pp. 1907-1914.
19. Thynell, S.T., Gongwer, P., and Brill, T.B., "Condensed-Phase Kinetics of RDX Derived from Model of T-Jump/FTIR Spectroscopy Method," *Journal of Propulsion and Power,* Vol. 12, No. 5, 1996, pp. 933-939.
20. Brill, T.B., "Multiphase Chemistry Considerations at the Surface of Burning Nitramine Monopropellants," *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 740-751.
21. Price, E.W., Bradley, H.H., Jr., Dehority, G.L., and Ibiricu, M.M., "Theory of Ignition of Solid Propellants," *AIAA Journal,* Vol. 4, No. 7, July 1966, pp. 1153-1181.
22. Hermance, C.E., "Solid-Propellant Ignition Theories and Experiments," *Fundamentals of Solid Propellant Combustion*, AIAA Progress in Astronautics and Aeronautics Series, Edited by Kuo, K.K. and Summerfield, M., Vol. 90, 1984, pp. 239-304.
23. Vilyunov, V.N., and Zarko, V.E., *Ignition of Solids*, Elsevier Science Publishers, NY, 1989.
24. Linan, A., and Williams, F.A., "Theory of Ignition of a Reactive Solid by Constant Energy Flux," *Combustion Science and Technology*, Vol. 3, 1971, pp. 91-98.
25. Linan, A., and Williams, F.A., "Radiant Ignition of a Reactive Solid with In-Depth Absorption," *Combustion and Flame*, Vol. 18, 1972, pp. 85-97.
26. Baer, S.D., and Ryan, N.W., "An Approximate but Complete Model for the Ignition Response of Solid Propellants," *AIAA Journal*, Vol. 6, No. 5, May 1968, pp. 872-877.
27. Bradley, H.H., "Theory of Ignition of a Reactive Solid by Constant Energy Flux," *Combustion Science and Technology*, Vol. 2, 1970, pp. 11-20.
28. Williams, F.A., "Theory of Propellant Ignition by Heterogeneous Reaction," *AIAA Journal*, Vol. 4, No. 8, Aug. 1966, pp. 1354-1357.
29. Bradley, H.H., and Williams, F.A., "Theory of Radiant and Hypergolic Ignition of Solid Propellants," *Combustion Science and Technology*, Vol. 2, 1970, pp. 41-52.
30. Andersen, W.H., "Theory of Surface Ignition with Applications to Cellulose, Explosives and Propellants," *Combustion Science and Technology*, Vol. 2, 1970, pp. 23-221.
31. Andersen, W.H., "Analysis of Ignition Behavior of M2 Propellants," *Combustion Science and Technology*, Vol. 5, No. 1, 1972, pp. 43-46.
32. Andersen, W.H., "Model of Transient Ignition to Self-Sustained Burning," *Combustion Science and Technology*, Vol. 5, No. 2, 1972, pp. 75-81.
33. Linan, A., and Crespo, A., "An Asymptotic Analysis of Radiant and Hypergolic Heterogeneous Ignition of Solid Propellants," *Combustion Science and Technology*, Vol. 6, No. 4, 1972, pp. 223-232.
34. Niioka, T., "Heterogeneous Ignition of a Solid Fuel in a Hot Stagnation Point Flow," *Combustion Science and Technology*, Vol. 18, No. 5-6, 1978, pp. 207-215.

35. Hermance, C.E., Shinnar, R., and Summerfield, M., "Ignition of an Evaporating Fuel in a Hot Oxidizing Gas, Including the Effect of Heat Feedback," *Astronautica Acta*, Vol. 12, No. 2, 1966, pp. 95-112.
36. Hermance, C.E., and Kumar, R.K., "Gas Phase Ignition Theory for Homogeneous Propellants Under Shock Tube Conditions," *AIAA Journal*, Vol. 8, No. 9, Sept. 1970, pp. 1551-1558.
37. Kumar, R.K., and Hermance, C.E., "Ignition of Homogeneous Solid Propellants Under Shock Tube Conditions: Further Theoretical Development," *AIAA Journal*, Vol. 9, No. 8, Aug. 1971, pp. 1615-1620.
38. Kumar, R.K., and Hermance, C.E., "Gas Phase Ignition Theory of a Heterogeneous Solid Propellant Exposed to a Hot Oxidizing Gas," *Combustion Science and Technology*, Vol. 4, 1972, pp. 191-196.
39. Kumar, R.K., and Hermance, C.E., "Role of Gas-Phase Reactions During Radiant Ignition of Solid Propellants," *Combustion Science and Technology*, Vol. 14, No. 4-6, 1976, pp. 169-175.
40. Liau, Y.-C. and Yang, V., "An Improved Model of Laser-Induced Ignition of RDX Monopropellant," *Proceedings of 33rd JANNAF Combustion Subcommittee Meeting*, CPIA Publication, Monterey, CA, November 4-8, 1996.
41. Gongwer, P.E., Arisawa, H., and Brill, T.B., "Kinetics and Products from Flash Pyrolysis of Cellulose Acetate Butyrate (CAB) at 460-600 °C," *Combustion and Flame* (accepted).
42. Mallery, C., and Thynell, S.T., "Species and Temperature Profiles of Propellant Flames Obtained from FTIR Absorption Spectrometry," *Combustion Science and Technology*, Vol. 122, No. 1-6, 1997, pp.113-129.

6. MULTI-BUBBLE PHENOMENA DURING IGNITION

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This portion was not covered during the workshop. However, I believe it is also closely linked to the ignition and flamespreading processes in granular propellant beds. It is known from various experimental evidence that a propellant under heating at low pressures could generate a foam layer on its heated surface. For RDX or RDX-based propellants, the two-phase phenomena in the surface region could lead to the generation of reactive chemical species in the foam layer, thereby affecting the overall ignition and flamespreading processes as well as influencing the low-pressure burning behavior of gun propellants.

In the following, I am listing some important points based upon our research findings from the paper entitled "Modeling and Numerical Simulation of Physicochemical Processes Occurring in the Two-Phase Foam Layer of Burning RDX" by K.K. Kuo, Y.C. Lu, and Y.S. Tseng, presented at the Fourth International Symposium on Special Topics in Chemical Propulsion, Stockholm, Sweden, May 27-31, 1996.

The two-phase phenomena in the surface region of RDX could have significant effects on the low-pressure burning rate and ignition behavior of RDX-based propellants. A model describing the physicochemical processes occurring in the two-phase foam layer of burning RDX was developed. An analysis based upon Lagrangian formulation, incorporating vaporization, heat transfer, and gas-phase chemical reactions was applied to a single bubble in the two-phase region. A multi-bubble analysis was also developed using a statistical treatment of families of single bubbles. The results of the single-bubble simulation indicate pronounced vaporization of RDX in the foam layer; however, very little decomposition of RDX occurs in the gas bubbles even though the growth of the bubbles is significant, and the gas bubble temperature is largely governed by the surrounding liquid temperature.

During combustion, RDX develops a complex flame structure, involving a gas-phase flame zone and a two-phase foam layer which develops on the surface of the solid RDX. The overall structure of a burning RDX monopropellant, was described by Kuo et al. [1]. The solid RDX first liquefies and then bubbles begin to nucleate in the liquid layer. The existence of a molten foam zone on the surface of burning RDX has been observed in several companion research studies. Many micrographs of the foam layer were obtained by Wilson et al. [2]. These micrographs of recovered XM39 and M43 composite propellants containing 76% RDX clearly showed the existence of bubbles in the foam layer.

Most of the earlier models of RDX combustion did not incorporate any detailed two-phase analysis of the foam zone, except the model of Li et al. [3], which offered a simplified treatment of this layer. The physicochemical processes occurring in the foam layer are of interest because heat release in the foam layer could play an important role in the ignition and combustion behavior of RDX. The recent model developed by Kuo and Lu [4] provided very

detailed analysis of the surface foam layer. In a parallel work, team members Liau and Yang [5] solved a simplified version of this model, with the consideration of void fractions in the surface reaction zone, and bypassed detailed treatment of bubble dynamics. The major objectives of this work are (1) to solve a portion of the comprehensive model developed by Kuo and Lu for simulating the physicochemical processes associated with a single bubble in the foam layer, (2) to extend the single-bubble analysis to a statistical description of multi-bubble phenomena in the two-phase foam layer, and (3) to incorporate this model of the two-phase foam layer into a comprehensive model of propellant combustion in the near future.

From the single-bubble results, several major observations are summarized below:

1. Similar to the physical situation observed by Wilson et al. [2], the model predicts a large amount of bubble growth at low pressures.

2. The amount of decomposition of RDX is quite small due to the relatively low temperature of the gaseous mixture inside the bubble.

3. The gas-phase reaction between CH_2O and NO_2 is negligible inside the bubble for the conditions considered, as evidenced by the low mass fractions of CO and CO_2 inside the bubble. This is due to the relatively low temperature of the gaseous mixture inside the bubble and the low concentrations of decomposition products CH_2O and NO_2 inside the bubble.

4. Due to effective heat transfer between the liquid and gas bubble, the gas bubble temperature is largely governed by the liquid temperature. This implies that for RDX-based composite propellants, if the RDX liquid can react exothermically with the binder melt in the foam layer of a burning propellant, the gas-phase reactions inside the bubble can easily be triggered by these exothermic reactions. Conversely, if the RDX liquid and binder melt react endothermically, the gas-phase reaction in the bubbles can be suppressed.

In brief, a detailed model of the physicochemical processes occurring in the two-phase foam layer of burning RDX monopropellant has been developed. This model considers the time history of one bubble from its nucleation to the instant prior to its bursting at the top surface of the foam layer. The single-bubble model has been solved numerically and extended to describe multi-bubble phenomena using a statistical treatment of families of single bubbles. The multiple-bubble model is being solved numerically and can be incorporated into a comprehensive model of RDX combustion in the future.

The modeling approach developed in this work could also be applied to other energetic materials besides RDX. With limited modification, this detailed foam layer analysis can be extended for prediction of nitramine-based composite propellants. Additionally, the complicated surface burning phenomena of liquid propellants (e.g., XM 46) could be treated with this approach.

6.1 References

1. Kuo, K. K., Litzinger, T. A., and Hsieh, W. H., "Interrelationship Between Solid-Propellant Combustion and Material's Behavior," Proceedings, Materials Research Society Symposium, Vol. 296, 1993, pp. 331-348.

2. Wilson, S. J., Fetherolf, B. L., Brown, P. W., and Kuo, K. K., "Surface Microstructure from Laser-induced Pyrolysis of M43 and XM39," Proceedings, 30th JANNAF Combustion Subcommittee Meeting, CPIA Publication, Vol. 11, November 1992, pp. 269-281.

3. Li, S. C., Williams, F. A., and Margolis, S. B., "Effects of Two-Phase Flow in a Model for Nitramine Deflagration," Combustion and Flame, Vol. 80, 1990, pp. 329-349.

4. Kuo, K. K. and Lu, Y. C., "Modeling of Physiochemical Processes of Burning RDX Monopropellant with Detailed Treatments for Surface Reaction Zone," Proceedings of the Twentieth International Pyrotechnics Seminar, Colorado Springs, Colorado, July 25-29, 1994, pp. 583-600.

5. Liau, Y. C. and Yang, V. "Analysis of RDX Monopropellant Combustion with Two-Phase Subsurface Reactions," Journal of Propulsion and Power, Vol. 11, No. 4, Jul-Aug 1995, pp. 729-739.

7. WORKSHOP DISCUSSION

The formal presentations of the first day of the workshop were followed by a half day of group discussion. The following questions provided stimulus and structure to the discussion. What systems are currently being addressed? What phenomena are now being modeled? What approximations are currently made to achieve tractability? What new phenomena should be modeled? What model systems might be valuable for confidence building? What are realistic expectations for these models?

The reader is reminded that the context of the workshop discussion was, as explained in the Introduction, Army-sponsored research in support of gun-propulsion technology problems. Much of the discussion, however, is equally applicable to the state of the art in fundamental combustion modeling for other applications as well.

7.1 What systems are currently being addressed?

At present the combustion of two solid energetic materials has been modeled at a level of detail which explicitly treats the fundamental physical processes and elementary chemical reactions, at least to some degree. These materials are frozen ozone (ARL code, section 4.5, Ref. 2) and RDX (Penn State code, section 5.4, Ref. 14). In addition, the groundwork is already being laid to include mixtures of the ingredients of the current Army nitramine gun propellants, XM39 and M43.

The work on frozen ozone was undertaken to explore the theoretical description of three-phase combustion on the most fundamental level without the distraction of the chemical complexities and uncertainties associated with RDX. The intent was to make as few assumptions and approximations as possible and carry over what is learned to the materials of more practical interest. This effort has led to an appreciation of the role of gas/surface reactions, nonideal mixture effects on the basic gasification/regression mechanism, thermodynamic critical phenomena, product-gas absorption by the surface, and liquid-phase molecular diffusion.

Modeling of the combustion of pure RDX with somewhat more idealized physical submodels than the ozone case has been conducted in parallel. This RDX modeling has broken new ground in describing the two-phase subsurface reaction zone. Bubbles have long been observed in decomposing liquid RDX. The approach taken here was to study the dynamics of bubble formation and growth in isolation and then incorporate this understanding into a comprehensive burning-rate model. The comprehensive model has been couched in a one-dimensional formalism using the concept of microscopic porosity, gas from subsurface RDX decomposition and evaporation being assumed to account for void formation and growth. This model affords the opportunity to study which chemical and physical processes most sensitively affect the burning rate and temperature sensitivity. The model has also been recently extended in capability to treat ignition and transient-combustion phenomena.

Experiments have already been initiated at Penn State to study the combustion phenomena associated with two-component mixtures, e.g., RDX/CAB, RDX/ATEC, RDX/NC, RDX/PU, and RDX/EP in a systematic way. (CAB = cellulose acetate butyrate, ATEC = acetyl triethyl citrate, PU = polyurethane, EP = energetic plasticizer) Modeling of these mixtures will follow when condensed-phase overall-kinetics schemes along with reaction coefficients have been worked out by means of thermolysis experiments such as T-jump/FTIR spectroscopy. Because of a lesser tendency to produce soot, it may be that mixtures with energetic plasticizers will be easier to describe theoretically and of more pragmatic interest.

7.2 What phenomena are now being modeled?

The intent of the elementary-process models being discussed here is to compute aggregate characteristics such as the burning rate without resorting to empirical descriptions of the subprocesses (such as the so-called pyrolysis law relating the linear or mass burning rate to the surface temperature in an Arrhenius-like expression). Because rigorous descriptions of these subprocesses, in many cases, are either prohibitively complex for direct incorporation into the burning-rate model or not yet available, some degree of semiempiricism is unavoidable. However, a key feature of these models is that the subprocesses are characterized independently of their role in the full combustion phenomena, i.e., no model parameters should be chosen solely because they result in agreement between calculation and measured burning rate. This policy admits the possibility of failure and the concomitant advances in understanding of the underlying mechanisms that may be revealed in a postfailure analysis.

The present capabilities of both the ARL and Penn State models are most conveniently summarized by dividing the discussion into the treatments used in each phase and at each phase boundary. There are some differences in the two models and this will be pointed out as appropriate.

The physics and chemistry of the gas phase are best known. Both codes have the capability of treating an "unlimited" number of elementary chemical reactions, convection, thermal conduction, molecular diffusion, and thermal diffusion. The last three transport processes may be optionally treated by approximate mixture-averaging rules or rigorous (low-density limit) multicomponent formulation. Thus far, only the ARL code has exercised this higher level of rigor (with its attendant computational burden).

The greatest differences between the ARL and Penn State codes is in their treatments of the condensed phases. Both codes have the capability for any number of condensed-phase chemical reactions, though only the Penn State code has exercised this capability since ozone is not thought to have condensed-phase reactions. The ARL code treats the solid and liquid phases as separate mathematical domains with solutions matched through the melt-interface boundary condition. Temperature-dependent properties are allowed in each phase. The Penn State code treats the condensed phase as solid and liquid domains but allows for the formation of gaseous voids arising from products of RDX decomposition and subsurface evaporation in the liquid domain. These voids are treated in an averaged way by defining a porosity parameter which

increases from deep within the condensed phase to the surface. This artifice allows retention of a one-dimensional formalism which is obviously desirable from a computational standpoint. Within the voids the RDX vapor pressure is assumed to be at the equilibrium value associated with the local temperature. The liquid and void temperatures at the same depth are assumed to be equilibrated. At present two parallel global reactions for the decomposition of condensed-phase RDX are considered, and the decomposition products from these reactions are assumed to react further by one global reaction. Paralleling the comprehensive model development at Penn State is a separate modeling effort (also at Penn State) to characterize the dynamics of single- and multiple-bubble growth for eventual incorporation into the comprehensive model.

Presently both ARL and Penn State codes treat the surface regression as primarily a nonequilibrium evaporation phenomena, the condensing flux of energetic molecules being less than the escaping flux due to the gas-phase reactive depletion of the vapor-phase energetic molecules. Both evaporation models are "single-component" in the sense that the RDX evaporation rate is assumed to dominate the total regression rate and the heat of vaporization of RDX is taken to be the pure-liquid value. The Penn State model has the option of an interfacial or in-depth absorption of radiant energy for comparison with laser-assisted combustion experiments.

The ARL model has the unique capability of treating heterogeneous (gas/surface) reactions. For the ozone case, including this process affected the burning rate to a negligible degree because of canceling effects, but the detailed heat-flux balances were significantly affected.

Finally, the Penn State model has been given the unique capability of time-dependent calculation, enabling it to be applied to both ignition and transient-combustion phenomena. This is a considerable enhancement and confers the potential for substantive tests of the code's predictive capability.

7.3 What approximations are currently made to achieve tractability?

The development of a comprehensive burning-rate model for solid energetic materials involves the interweaving of many different scientific disciplines. Because of this inherent eclecticism, a clear perception of all the approximations being made comes only by degrees. Some approximations are introduced consciously and some may be implicit in a given point of view or approach. This discussion question was intended to bring to light both of these kinds of approximations. Thus, some implicit approximations might not be strictly an issue of tractability at all and might easily be removed or improved on recognition.

Again organizing the discussion by phase, a good start has been made at developing a kinetic mechanism to describe the primary flame zone of pure RDX and possibly HMX. However, many of the rate coefficients have only been estimated theoretically and there is little experimental verification of the mechanism at the high-heating rates encountered under self-sustained combustion. The dark-zone mechanism is better understood than the primary zone, but confidence is higher in the dark-zone mechanism for nitrate-ester propellants than for nitramine

propellants. Verification of the nitramine dark-zone mechanism is still sufficiently inexact that some rate coefficients may be in error and some important reaction may even be missing. The gas-phase reaction set needs to be scrutinized further. A separate issue is the applicability of the low-density transport equations at the higher pressures. The currently coded equations presume that binary collisions predominate, however, theoretical predictions of burning rate at pressures up to 6000 atm are of interest to the gun application. Critical pressures for many gases are in the tens of atm. Thus even at pressures as low as 50 atm, density effects may be significant. Little attention has been given to assessing these problems and improvements will undoubtedly be difficult to effect. Nonideal equations of state have long been used in equilibrium thermochemical calculations of combusted-propellant gases; no detailed burning-rate model has yet incorporated them, but this would be relatively easy to change.

In the condensed phase there is some concern about the present use of global reactions for RDX. This type of description has proven to be hazardous in the gas phase; there is no reason to believe it will be less so in the condensed phase. A global description of the condensed-phase decomposition, while currently unavoidable, is also not commensurate with the level of detail modeled in the gas phase. There is an urgent need to develop fundamental theoretical models of the chemistry and physics of the condensed phase as well as experimental tools for characterizing the subsurface region. A related concern is the validity of the porosity concept for describing the complex three-dimensional foam zone.

Finally, a host of problems present themselves with respect to the description of interfacial phenomena. The absorption of secondary gases into the surface is currently ignored; allowing it may necessitate treating molecular diffusion in the liquid layer. Heats of desorption or evaporation as well as evaporation rates themselves can be significantly affected by the presence of other molecules and by increases in pressure. Introduction of pressure-corrected multicomponent mixture properties may be necessary and entail considerable additional complexity. Finally, there is some evidence that the physical ejection of matter from the burning surface of RDX may be occurring. Obviously, if this is an important process, it will be difficult to describe accurately.

7.4 What new phenomena should be modeled?

This question was intended to draw a consensus from the group concerning which of the approximations identified under section 7.3 were likely to be of such significance that attempts to include them should be undertaken. However, the burning rate is such a highly integrated process that it is difficult or impossible to predict which subprocesses will ultimately prove to be important. No attempt was made, therefore, to assign priorities to improving the identified approximations.

One potentially significant phenomenon, not currently modeled or under investigation is related to what one might call the preignition gasification period. During this period the propellant is not yet undergoing self-sustained combustion but is being subjected to convective heating by the igniter and/or flamespreading flux. There may be appreciable pyrolysis of the propellant surface during this period, releasing primary-zone reactants (such as CH_2O, N_2O,

HCN, NO_2, etc.) or even more complex chemical species into the general flow field. These species, if in sufficient abundance, could affect the distribution in time and space of the chemical heat release. Experiments to characterize this phenomenon would, therefore, be valuable.

A number of phenomena not previously modeled at the detailed-kinetics level were suggested. These included radiative energy loss from the surface, radiative energy gain by the surface from the flame zone, convective burning in porous materials and in macroscopic pores, convective ignition, erosive burning, grain-to-grain sympathetic combustion, and possibly 3-D effects involving the foam layer and heterogeneous propellants.

7.5 What model systems might be valuable for confidence building?

Recognizing that these models are just too complex to "validate" in anything more than a very limited fashion, the best one can do is to gain confidence in the submodels by application to a variety of systems of increasing complexity. The following energetic materials were proposed as suitable to this purpose: hydrogen peroxide (H_2O_2), hydrazine (N_2H_4), nitromethane (CH_3NO_2), methyl nitrite (CH_3ONO), methyl nitrate (CH_3ONO_2), ethyl nitrite (C_2H_5ONO), ethyl nitrate ($C_2H_5ONO_2$), and perhaps an organic molecule with more than one ONO_2 group to enable self-oxidation. A combined experimental and theoretical effort on these "model" systems could allow assessment of the reliability of basic submodel treatments by observing them in different contexts. Since some of these "simple" systems also exhibit two-stage flames, they would provide an opportunity to test our understanding of propellant dark zones, which are of vital interest to interior ballistics.

Group opinion on the value of these studies, in the face of current funding limitations, was mixed. Some felt that this work, in diverting resources away from energetic materials of practical interest, would slow overall progress toward the goal of addressing propellant combustion. An additional complication is the apparent commercial unavailability of many of the proposed compounds, making the further step of test-material synthesis a necessity. Although initiating a new experimental effort on these materials proved controversial, it was generally agreed that a theoretical-only effort would be worthwhile since many of these systems have been the subject of previous experimental work.

7.6 What are realistic expectations for these models?

It was generally thought that, at the very least, these models would prove valuable in assessing the relative importance of various mechanisms, e.g., the relative role played by evaporation and reaction in determining burning rate. In addition, the models should be able to rationalize gross combustion features such as slope breaks in the burning rate. However, beyond these traditional roles, the rapidly increasing sophistication in quantum theoretical methods gives a newly justified promise of the a priori capability to predict burning rates. The advent of this capability, of course, would revolutionize the development of tailored, high-performance gun propellants.

7.7 Discussion Summary

The discussion period served to highlight the current capabilities and limitations of the current combustion codes. Group consensus on the exact path to future code refinements was not achieved; however, this outcome is perhaps natural, the paths being dependent on personal enterprise and skill mix. Nonetheless, the workshop provided an articulation of the current and future needs of the interior-ballistic models. These needs give valuable guidance in making decisions on refinement priorities. For example, the dark zone plays an important role in the ignition delays observed in guns. Therefore, a priority exists for accurately describing combustion phenomena below about 20-30 atm. This would argue for postponing serious concerns about high-density-gas effects. High loading densities will also be a fact of life in new high-performance gun systems. This may give impetus to studies of sympathetic combustion between adjacent grains.

8. WORKSHOP SUMMARY POINTS

- **Future Directions in Army Large-Caliber Gun Propulsion**
  - Solid propellants continue to be attractive because of their high energy density and reliable means of controlling rate of energy release.
  - Future propellants will employ new high-energy-density materials now being synthesized and tested.
  - Achieving future performance goals will require high-loading-density propelling charges with their attendant ignition difficulties, including transient combustion excursions that can potentially lead to catastrophic pressure waves.
  - Future systems may employ plasma igniters.
  - Future systems may employ direct laser ignition.
  - Weapons will function at a high rate of fire, requiring autoloaders and, in turn, rigid combustible cases, which can influence ignition and flamespreading.

- **Interior-Ballistic Modeling Challenges**
  - Next-Generation IB code (NGEN) has modular structure to treat multiple propulsion concepts.
  - Simulating behavior of combustible cases will be difficult.
  - High-loading-density charges may present special difficulties in treating transient shear flow with heat release driven by finite-rate chemistry.
  - NGEN couples multiphase convective flow with a multispecies finite-rate chemical combustion mechanism.
  - For numerical tractability NGEN utilizes a reduced-set chemical-reaction description of propellant dark-zone chemistry to model ignition delays.

- **State of Understanding in Combustion Chemistry**
  - The dark-zone chemistry is thought to be responsible for the longer ignition delays in guns observed for nitramine propellants.
  - Dark-zone chemical mechanism and rates are now reasonably well known - with higher confidence for double-base propellants than for nitramine propellants.
  - A reduced dark-zone chemical mechanism has been developed for IB-code use.
  - Outlines of primary reaction-zone chemistry are in hand but details need more work to confirm.
  - Sensitivity analysis shows which reactions are most influential, guiding allocation of experimental resources toward the most critical steps. Because of this, the reaction mechanisms and rates must be continually updated as new data become available.
  - Much work remains to develop descriptions of condensed-phase physics and chemistry.

- **State of the Art in Combustion Models**
  - Work during the past ten years in chemical kinetics, spectroscopy, theoretical calculations, and modeling has enormously increased understanding of propellant ignition and combustion, enabling the current chemically specific combustion models.
  - Three-phase combustion models with detailed kinetics and evaporative regression mechanisms now exist for volatile energetic materials like RDX.
  - Combustion of pure RDX has included a two-phase foam zone based on a variable-porosity concept.
  - Bubble growth and dynamics are being studied separately for later inclusion as a submodel in the RDX model.
  - Relatively simple systems such as frozen ozone are being studied to clarify the reliability of fundamental assumptions.
  - Time dependence has recently been added to detailed combustion models, allowing study of ignition and transient-combustion behavior.
  - The goal of predicting the burning rate of a propellant from its ingredients now appears to be reachable. This would revolutionize development of new propellants and, coupled with the IB model, the development of optimized propelling charges.

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13. ABSTRACT *(Maximum 200 words)*

A workshop with the objective to view the current state of the art of energetic-material combustion models within the context of future requirements of gun interior-ballistics (IB) models was held at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground, MD, on 9 and 10 April 96. The workshop was motivated by the recognition that modeling and simulation will be an essential cost-saving and time-saving tool in the design, development, testing, and evaluation of future gun-propulsion systems, and that, under current funding constraints, research on the underlying fundamentals must be carefully directed toward the most critical technology barriers. To facilitate this process, a perspective was presented on the fundamental physics and chemistry currently utilized in IB codes (XKTC, etc.) and the extensions planned for advanced codes (the NGEN family). The state of the art in fundamental descriptions of energetic-material combustion was then summarized and discussed with the intent of giving focus to those issues that could impact the future development needs of the IB research community.

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