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# SOLID REACTANTS FOR FLUORINE GAS GENERATORS

C. E. Fogle, et al

United Technologies Corporation

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# SOLID REACTANTS FOR FLUORINE GAS GENERATORS

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A program has been conducted to explore the possibility of using solid reactants, other than those currently under consideration, for the preparation of fluorine equivalent gas (F, $F_2$, or $NF_3$) and to evaluate the potential of promising candidates. A list of 32 candidates was compiled which was reduced to 3, $KBrF_6$, $KClF_4$, and $LiMnF_5$, by applying pre-established selection criteria based on toxicity, cost, safety, vapor pressure or melting point, and others.

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Excellent properties and performance were obtained from a formulation based on $KBrF_6$ yielding approximately 13% by weight equivalent fluorine (18 percent by weight active fluorine) with a potential of over 25 percent active fluorine through composition variation. This approach was abandoned owing to the lack of information related to the effect of the species BrF on HF-DF laser output. Similarly, although equally good properties and performance could be obtained, $KClF_4$ formulation evaluation was discontinued when it became known that ClF has a deleterious effect. The third candidate, $LiMnF_5$, offers the possibility of the production of pure fluorine albeit at relatively low yield (about 10 weight percent) and investigations of its formulations have been pursued.

## SUMMARY

A series of available or known solid reactants capable of generating fluorine when combined with fuels was identified and examined during the course of the program.

An extensive literature review combined with a thermochemical evaluation procedure defined candidates with labile fluorine that were subsequently screened as to acceptability in meeting specified requirements. A series of 32 candidate fluorine reactants was included in the reactant screening and rating operations. The parameters that had major influence on reactant acceptability during this screening operation were stability, safety, and cost.

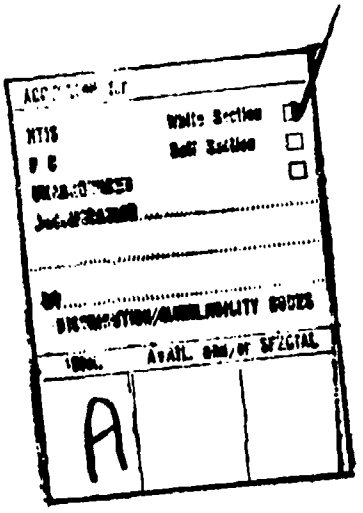
A series of five reactants was selected for experimental evaluation based on the reactant ratings. The compounds were $NOBrF_4$, $(NO)_2MnF_6$, $KBrF_6$, $KClF_4$, and $LiMnF_5$. The first two reactants, $NOBrF_4$ and $(NO)_2MnF_6$, were eliminated from consideration at an early stage because of the low fluorine yield of $(NO)_2MnF_6$ and the expected detrimental influence of NOF and bromine products on laser prformance in the case of $NOBrF_4$. The two interhalogen derivatives, $KBrF_6$ and $KClF_4$, were carried through small-scale grain testing (10 to 20 g). Test data showed the $KBrF_6/Mg_3N_2$ and $KClF_4$/AlN reactant systems to be most amenable to ignition and combustion in the scale tested. Studies of these two reactant systems were discontinued based on the anticipated detrimental effects of BrF and ClF on laser performance.

Work on $LiMnF_5$ was conducted based on prediction of fluorine as the only gaseous product with other products forming a sintered residue. Ignition and combustion of various $LiMnF_5$ and fuel reactant systems were difficult to achieve on the scale tested. The most promising candidate based on the grains tested consisted of a $LiMnF_5$/Mg formulation.

An exploratory analysis and design of a fluorine gas generator system were developed using the $LiMnF_5$/Mg reactant system parameters as input. The primary area of uncertainty was in the ignition train design.

## PREFACE

The investigation of solid reactants for fluorine gas generation reported herein was performed by the Chemical Systems Division of United Technologies Corporation under contract No. N60921-75-C-0224. Inclusive dates for the technical effort on this program were 2 June 1975 to 2 February 1976 and the final report was submitted on 15 March 1976. Dr. R. O. MacLaren was the program manager and Dr. J. D. Breazeale was the project scientist. Significant contributions to this program were made by Mr. C. E. Fogle and Mr. D. R. Matthews. The contributions and consultations of Mr. B. G. Pallay, Dr. C. Boyars, and Mr. R. Bardos of NSWC are gratefully acknowledged.



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# INTRODUCTION

This document describes the investigations performed under NSWC contract No. N60921-75-C-0224, "Solid Reactants for Fluorine Generation." The overall objectives of the program were to select, by approved screening and selection criteria, and to evaluate by tests and analysis, solid reactants and approaches capable of producing F, $F_2$, or $NF_3$ at weight yields corresponding to 10% equivalent fluorine with an ultimate goal of 25% equivalent fluorine. Furthermore, the reactant systems and approaches selected should be capable of producing an exhaust containing minimum levels of contaminants or particles and the system should be scalable to produce 0.25 lb of fluorine per second for up to 5 sec duration.

Principal operational constraints in development of a DF chemical laser are the storing, handling, and safety of the reactants. These constraints emphasized the desirability of solid gas generators to produce the gaseous reactants needed for HF/DF lasers. With demonstrated practical generation of $H_2$ and $D_2$ from solid formulations and since stored helium, nitrogen, or nitrogen-generating formulations can be used as the diluent gas source, the primary remaining problem area is that of a suitable fluorine source.

The hazardous nature and physical properties of fluorine combine to make its storage in the elemental form a formidable undertaking if substantial quantities are to be stored for extended periods. The problems of corrosivity during the storage period, the potential of boiloff or leakage of the liquid phase when employed as a cryogenic reagent, and the need to supply a pressurization subsystem are drawbacks to liquid fluorine. The inherent storability of solid reactants makes the approach of solid grains for fluorine generation attractive, and has been the primary impetus for work in this area.

Although several fluorine-generating formulations have been characterized to date on a laboratory scale, there is currently no fully developed composition based on available reactants which produces F, $F_2$, or $NF_3$ as combustion products. Among the reactants which have been investigated



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as fluorine generation sources are the xenon fluorides, $XeF_2$ and $XeF_4$, and the $NF_4^+$ salts, $NF_4BF_4$ and $NF_4SbF_6$. The xenon fluorides exhibit marginal stability characteristics, particularly for Navy usage. The higher fluorine content compounds, $NF_4BF_4$ and $NF_4SbF_6$, are presently not available at reasonable cost in quantities sufficient for large-scale operations.

The program reported herein is an investigation of alternative approaches for generation of gaseous F, $F_2$, and $NF_3$ by means of solid reactants based on available, relatively inexpensive ingredients. The availability and low cost requirements were imposed to provide a trade-off option to the higher cost tetrafluoroammonium salts. In addition, constraints on the gaseous product composition were imposed such that it would be acceptable for DF laser operation. Finally, the requirements included practical guidelines relating to handling and safety.

The program developed to meet these objectives was divided into three consecutive tasks: task 1, screening and selection of reactants and approaches; task 2, characterization and testing of the selected reactant systems; and task 3, scalability testing and supporting analysis. The program plan provided for specification of five candidate reactants at the end of screening studies of task 1, selection of three candidates to be evaluated during the testing effort of task 2, and up to two candidates for the task 3 scalability testing and supporting analysis.

Synthesis studies performed as part of the IR&D program yielded a portion of the reactant materials used in the task 2 efforts. For completeness, the results of these studies have been included in this report where appropriate.

## PROGRAM DISCUSSION

Several requirements for a gas generator producing predominantly gaseous fluorine can be defined. A primary guideline is production of gas generator products that approach, or match, the composition of gases currently being used in laser operations (i.e., fluorine, fluorine-helium, or fluorine-nitrogen mixtures). Achievement of this guideline allows more ready transition from lasers employing gaseous fluorine to solid generator operated lasers.

Throughout the program, a set of requirements was considered that imposed limits on acceptability of various physical, chemical, and economic properties of candidate reactants. These requirements, while subjective in certain areas, were intended to ensure that the final reactant systems (fluorine gas generators) would have utility in an end-item application. The minimum requirements that need to be satisfied for both the fluorine reactants and reactant systems are as follows:

A. Yield of fluorine (as F, $F_2$, and $NF_3$) of 10 weight percent (minimum) to 25 weight percent (goal).

B. Reactants are stable solids (and nonvolatile) at temperatures up to 50 C.

C. Reactants are available from commercial sources or can be synthesized by practical synthesis routes.

D. Once ignited, reactant systems sustain a controlled combustion.

E. Minimum concentrations of undesirable or unacceptable gases are produced upon combustion:

   (1) Acceptable - $N_2$, $O_2$, He, Ar, $CF_4$, and $SF_6$

   (2) Undesirable - HF, DF, $CO_2$, $COF_2$, $SO_2F_2$, and $ClF_3$

   (3) Unacceptable - Fluorine reactive gases

F. Reactants and fluorine gas generator formulations have normal handling characteristics:

   (1) Low sensitivity to impact, friction, and spark

   (2) Autoignition temperature (AIT) in excess of 120 C

   (3) Low toxicity of reactants

   (4) Storable at normal temperatures

(5) Capable of being processed in large scale.

G. Particulate matter can be removed from generated gas.

Of the noted requirements, those having the greatest impact on the selection of reactants were the fluorine content (item A) and availability (item C), whereas the selection of reactant systems for evaluation was constrained primarily by the presence of other gases in the products (item E) and achieving sustained combustion (item D). The last item, elimination of condensed solids from the exhaust, is dependent upon the formulation and end use approach.

The three basic approaches to producing a solids-free exhaust in the fluorine gas generators were all considered in the course of the selection process conducted in this program. The first approach follows conventional gas generator technology by formulation of compositions whose products are all gaseous, e.g., the early formulations of $NF_4BF_4$ with tetrafluoroethylene[1] are typical of this approach. This type of formulation has the advantage of not requiring separation of condensed products from the gas phase but tends to produce excessive gaseous contaminant levels. The second approach considered in the program is an adaptation of the well-established chlorate candle technology[2] to develop formulations that produce a sintered solid under certain definable conditions. Previous studies have shown that, provided the ratio of the liquid-to-solid phases is controlled, good separation of gases from the condensed phases occurs. A small filtration unit normally has been required to remove the last vestiges of condensed particles. Excessive amounts of a liquid phase have been found to cause slumping problems on scale-up.[3] This second type of generator generally provides a lower fluorine yield, based on total gas generator weight, but produces a gaseous product with a higher fluorine content. The use of the sintered residue approach for fluorine generators has been reported in work using $NF_4SbF_6$[4] and $NF_4BF_4$[5]. The third approach also allows formation of solid- or liquid-phase combustion products but does not produce a sintered residue. In this approach, a second subsystem is required to remove the condensed products. The complexity of this subsystem is dependent upon the combustion temperature and

the quantities and physical characteristics of the condensed, and condensable, combustion products. This third type of system is potentially adaptable to an accumulator approach for multipulse operation.

The following sections present the overall approaches taken to evaluate alternative solid reactants for fluorine generators; the results of the theoretical, experimental, and design studies based on the selected approaches; and a discussion of the results.

## TASK 1: SCREENING AND SELECTION OF CANDIDATE REACTANTS AND APPROACHES

The objective of this task was to survey potential fluorine source candidate reactants, subject these candidates to a set of approved screening criteria, and select and recommend the most appropriate reactants for subsequent testing. A reactants considered list was prepared to summarize the results of task 1. A minimum of five reactant systems was selected for consideration in the testing phase (task 2) which follows this section.

The initial step in the screening and selection process consisted of a thorough literature search, including the use of automated information retrieval services, for all compounds having a potential for release of at least a portion of their fluorine on thermal excitation. This literature search resulted in identification of in excess of 60 candidate compounds for later evaluation in the program. (Pertinent literature is listed in the bibliography as references 6 through 45.)

The stability of a selected set of gaseous fluorides was evaluated from thermodynamic considerations to serve as a guideline in the selection of materials which possess weakly bound fluorine or form species with weak bonds to fluorine and therefore decompose readily. The equilibrium decomposition temperature for these species, tabulated in table 1, was calculated as the temperature at which log $K_p$ was approximately zero.

Temperature limitations were imposed on the evaluation by end-use application. In the case of a DF laser, the lower limit is that required to dissociate $F_2$, approximately 1300 K, while the upper limit is imposed by

TABLE 1. RELATIVE STABILITY OF GASEOUS SPECIES CONTAINING FLUORINE

| Species | Decomposition Reaction | Decomposition[a] Temperature, (K) |
|---|---|---|
| $ClF_5$ | $ClF_5 \longrightarrow ClF_3 + F_2$ | 500 |
| $NOF_3$ | $2NOF_3 \longrightarrow N_2 + O_2 + 3F_2$ | 600 |
| $IF_7$ | $IF_7 \longrightarrow IF_5 + F_2$ | 600 |
| $NO_2F$ | $2NO_2F \longrightarrow N_2 + 2O_2 + F_2$ | 750 |
| $ClF_3$ | $ClF_3 \longrightarrow ClF + F_2$ | 800 |
| $NF_3$ | $2NF_3 \longrightarrow N_2 + 3F_2$ | 900 |
| $BrF_5$ | $BrF_5 \longrightarrow BrF_3 + F_2$ | 1000 |
| NOF | $2NOF \longrightarrow N_2 + O_2 + F_2$ | 1200 |
| $F_2$ | $F_2 \longrightarrow 2F$ | 1300 |
| $BrF_3$ | $BrF_3 \longrightarrow BrF + F_2$ | 1500 |
| $SF_6$ | $SF_6 \longrightarrow SF_4 + F_2$ | 2100 |
| $IF_5$ | $IF_5 \longrightarrow IF_3 + F_2$ | 2600 |
| $SO_2F_2$ | $SO_2F_2 \longrightarrow SO_2 + F_2$ | 3500 |
| $PF_5$ | $PF_5 \longrightarrow PF_3 + F_2$ | 3800 |
| $SF_4$ | $SF_4 \longrightarrow S + 2F_2$ | 4100 |
| $SOF_2$ | $2SOF_2 \longrightarrow 2S + O_2 + 2F_2$ | 4500 |
| $PF_3$ | $PF_3 \longrightarrow PF + F_2$ | >6000 |
| $CF_4$ | $CF_4 \longrightarrow C + 2F_2$ | >6000 |
| $BF_3$ | $2BF_3 \longrightarrow 2B + 3F_2$ | >6000 |
| $COF_2$ | $2COF_2 \longrightarrow 2C + O_2 + 2F_2$ | >6000 |
| ClF | $2ClF \longrightarrow Cl_2 + F_2$ | >6000 |
| BrF | $2BrF \longrightarrow Br_2 + F_2$ | >6000 |
| IF | $2IF \longrightarrow I_2 + F_2$ | >6000 |
| PF | $2PF \longrightarrow 2P + F_2$ | >6000 |

[a] Temperature where log $K_p$ is near zero.

nozzle processes or materials consideration and is of the order of 2500 K. Therefore, those species whose dissociation occurs at temperatures less than 2500 K will have the most utility in the application, whereas those species which decompose at higher temperatures will remain intact at operational temperatures and do not represent sources of available fluorine. The emphasis on the dissociation of species, especially into F atoms, arises from the energetics of the DF laser system which cause the overall system performance to suffer if even the energy of dissociation for $F_2$ must be supplied internally.

It is apparent from table 1 that fluorine bonded to nitrogen is available, since all nitrogen-bonded species ($NOF_3$, NOF, $NO_2F$, and $NF_3$) decompose below the operating temperature of the laser combustor. Conversely, boron, phosphorus, carbon, and sulfur are not desirable as fluorine carriers since their polyfluorides are stable above the operating temperature. Of the interhalogens, chlorine and bromine can be expected to dissociate to the monofluorides; however, iodine clearly would result in formation of $IF_5$ as a stable product gas. The relative stability of the gaseous fluorides then is reflected in the fluorine yield values of candidate reactants. Armed with this information, the fluorine-containing compounds collected in the literature review were subjected to a preliminary screening to eliminate those without labile fluorine. A value of 10 weight percent available fluorine was imposed as an absolute lower limit of acceptability; however, for use in operational systems, a more practical value of 20 weight percent was employed.

Reactants Considered List

The reactants considered list (RCL) was compiled from all the candidate materials which remained after the preliminary review. In addition, several of the current $NF_4^+$ candidates were included for comparison bringing the list to a total of 32 materials to be evaluated. The RCL was subdivided into a set of five tables according to the nature of the properties to be tabulated. The various tables, the data contained thereon, and the basic source of information are summarized in table 2. The individual tables making up the RCL are compiled in appendix A.

TABLE 2. REACTANTS CONSIDERED LIST

| Table | Title | Data | Source |
|---|---|---|---|
| RCL-1 | Fluorine yield of reactants | Weight percent F at 300, 1000, 1500, 2000 K and $\gamma$ at 1500 K | Thermochemical calculations |
| RCL-2 | Stability of reactants | Physical properties, $\Delta H_f^\circ$, decomposition temperature, chemical reactivity | Technical literature |
| RCL-3 | Reactant availability and cost | Availability, synthesis routes, cost in 10-, 100-, 1000-, and 10,000-lb lots | Technical literature, chemical suppliers |
| RCL-4 | Reactant safety | Reactivity with air, precursor and decomposition product toxicity | Technical literature |
| RCL-5 | Reactant system performance | Weight percent F and $\gamma$ for candidate formulations | Thermochemical calculations |

Reactant Screening Procedure

The screening and selection process initially included the consideration of three approaches to the reactant systems based on the nature of the products of the generator. The first produces all gas products, the second produces a condensed phase which is retained as a residue and an easily filterable gas, while the third produces a gas with a relatively large fraction of condensed phase either entrained or formed during cooling. During the course of the program, attention was directed toward the second approach, i.e., reactants forming a sintered solid and a low solids content gas.

To evaluate the relative merits of the candidate reactants and reactant systems, a set of ranking criteria and weighting factors were established. These are tabulated in table 3. Five categories were established with each major category subdivided into related considerations.

The criteria incorporated those factors which would be expected to lead to a reasonably priced solid reactant system capable of delivering an adequate supply of fluorine gas free of excess contamination and with a minimum of hazards associated with its manufacture and use. A major consideration was the available fluorine content, initially of the reactant itself but ultimately of the reactant system which will produce the gas. This overall factor was given a weight of 25 out of a total of 100, divided 10 points for the reactant fluorine content and 15 points for gas generator fluorine content. The acceptable lower limit was designated as 20 weight percent for the reactant fluorine content and as 10 weight percent for the gas generator fluorine content. This differential was established to account for the consumption of reactant available fluorine by fuels incorporated in the candidate formulations.

The availability of the reactants or precursors and well-established synthesis routes were important considerations related to the cost of the constituents of the gas generator. These factors were combined as the second major criterion with a weighting factor of 20, divided equally between

TABLE 3. RANKING CRITERIA AND WEIGHTING FACTORS

| Criterion | Weighting Factor | Value Limit |
|---|---|---|
| Available fluorine content | 25 | |
| Reactant fluorine content | (10) | >20 weight percent F |
| Gas generator fluorine content | (15) | >10 weight percent F |
| Availability and cost | 20 | |
| Availability | (10) | Synthesis established |
| Cost | (10) | <$10/g for 10 lb |
| Stability, toxicity, and safety | 35 | |
| Reactant stability | (10) | >50 C |
| Reactant and product toxicity | (10) | Noncumulative |
| Safety of reactant system | (15) | Impact > 10 kg-cm |
| Product contamination by particles or deactivating species | 15 | To be defined |
| Ignitibility and combustion stability | 5 | Ignition by hot wire |

availability and cost. No definable limit was established for availability; a cost limit of less than $10 per gram in small scale was taken as a guideline.

Of vital concern was the safety, stability, and toxicity of the reactants, the processing characteristics of the reactant system and its stability as a gas generator. The third criterion of stability, toxicity, and safety was given a weighting factor of 35, the greatest weight of all criteria. This factor was subdivided into the three considerations with safety taking the predominant portion. This weighting was established based on previous safety constraints for shipboard operations. The acceptable lower limit of reactant stability was taken as 50 C (122 F). Reactants were ruled unacceptable if they or the products of combustion exhibited a chronic toxicity. A value of 10 kg-cm was established as the lower acceptable limit for impact sensitivity.

The degree of contamination of the product with solid particulate matter or with deactiving species would have a major impact on the value of candidate reactant systems in laser applications. This criterion was given a weighting factor of 15; however, since these parameters are difficult to define before test operations, this criterion had little effective impact on the selection process. Similarly, ignitability of the reactant system was also a factor to be considered in the system selection since a self-sustaining reaction must be initiated; however, determination of this criterion required extensive test data, not available on many reactants during screening.

The procedure used for the selection of the candidate reactants for ranking involved classification of the reactants as to acceptability in meeting the minimum requirements and those that were unacceptable on one basis or another. This classification is shown in table 4 for the 32 candidates. This tabulation was taken from the reactants considered list (appendix A) where the basis for the lack of acceptability is noted as an X on the RCL tables and, similarly, on the classification of reactants table. Those factors denoted by a parenthesized X were deemed marginal but this

TABLE 4. CLASSIFICATION OF REACTANTS

| Reactant No. | Reactant Composition | Ref. | F, (weight percent) | Cost | Physical Properties | Reactivity/ Safety | Availability | Acceptable |
|---|---|---|---|---|---|---|---|---|
| 1 | $NF_4BF_4$ | 6 | - | X | - | - | X | No |
| 2 | $XeF_6$ | 7 | - | (X) | (X) | X | (X) | No |
| 3 | $2NOF \cdot XeF_6$ | 8 | - | (X) | - | X | (X) | No |
| 4 | $KrF_2 \cdot XeF_6$ | 9 | - | (X) | - | X | (X) | No |
| 5 | $NOClF_4$ | 10,11 | - | - | X | - | - | No |
| 6 | $4XeF_6 \cdot MnF_4$ | 12 | - | (X) | - | X | (X) | No |
| 7 | $4XeF_6 \cdot SnF_4$ | 13 | - | (X) | - | X | (X) | No |
| 8 | $NOF \cdot XeOF_4$ | 14 | - | (X) | (X) | X | (X) | No |
| 9 | $XeF_2 \cdot BrF_5$ | 15 | - | (X) | X | - | (X) | No |
| 10 | $XeF_6 \cdot BF_3$ | 16 | - | (X) | - | X | (X) | No |
| 11 | $NF_4AsF_6$ | 17,18,19 | - | - | - | X | - | No |
| 12 | $(NO)_2MnF_6$ | 20 | - | - | - | - | - | Yes |
| 13 | $KBrF_6$ | 21 | - | - | - | - | - | Yes |
| 14 | $NF_3O \cdot SbF_5$ | 22,23 | - | - | - | - | (X) | Yes |
| 15 | $NOBrF_4$ | 24 | - | - | - | - | - | Yes |
| 16 | $XeF_2 \cdot XeF_4$ | 25,26 | - | - | - | X | (X) | No |
| 17 | $BrF_6AsF_6$ | 27,28,29 | - | - | - | X | - | No |
| 18 | $NOAsF_6$ | 44,45 | - | - | - | X | - | No |
| 19 | $NF_4SbF_6$ | 33,34 | - | - | - | - | - | Yes |
| 20 | $N_2F_3AsF_6$ | 35 | - | (X) | - | X | - | No |
| 21 | $RbBrF_6$ | 21 | - | - | - | - | - | Yes |
| 22 | $KClF_4$ | 21 | - | - | - | - | - | Yes |

TABLE 4. (continued)

| Reactant No. | Reactant Composition | Ref. | F, (weight percent) | Cost | Physical Properties | Reactivity/ Safety | Availability | Acceptable |
|---|---|---|---|---|---|---|---|---|
| 23 | $ClF_2BF_4$ | 40 | – | – | X | – | – | No |
| 24 | $ClF_3O \cdot BF_3$ | 41 | – | – | – | – | – | Yes |
| 25 | $CsBrF_6$ | 21 | – | – | – | – | – | Yes |
| 26 | $XeF_2$ | 37 | – | (X) | (X) | – | (X) | Yes |
| 27 | $NCVF_6$ | 30 | X | – | – | (X) | – | No |
| 28 | $XeF_2 \cdot MnF_4$ | 36,37 | X | (X) | – | – | (X) | No |
| 29 | $XeF_2 \cdot VF_5$ | 38,39 | X | (X) | – | (X) | (X) | No |
| 30 | $MnF_4$ | 31,32 | X | – | (X) | – | – | No |
| 31 | $LiMnF_5$ | 31 | X | – | – | – | – | No |
| 32 | $KMnF_5$ | 42,43 | X | – | – | – | – | No |

classification did not eliminate that reactant from consideration. The final column in table 4 depicts the state of acceptability which was used as the guideline in elimination of candidate reactants from further consideration.

After elimination of the candidates which were found unacceptable under any of the criteria, the remainder were compiled for rating according to the criteria discussed earlier. The rating for each criterion was from 0 to the maximum value of the weighting factor. Although the rating of each reactant or system within each of the criteria was subjective, the rating was derived by comparison with the other candidates. The summation of the ranking criterion values led to a score for each candidate and a subsequent ordering and identification of the most promising of the candidates.

The reactants, their ratings in the various areas, and their cumulative ratings are shown in table 5. The candidates are arranged in order of their cumulative ratings. Reactants currently under investigation were also included for comparison purposes. The reactants $NF_4BF_4$ and $LiMnF_5$ were considered marginal because of a low rating in the area of availability and cost for the former and fluorine content for the latter.

The fluorine content ratings were made based on a rating value-fluorine content correlation plot. This plot gave the highest rating of 25 to reactants having 40 weight percent fluorine or greater, and a rating of 0 for compounds having 15 weight percent fluorine or less. The cost factor was also derived from a rating value-cost correlation plot with the highest value (20) allotted to reactants with costs of \$30/lb or less in 10,000-lb lots. The other factors were defined more subjectively. The stability-safety criterion was based primarily on cumulative toxicity which downrated the antimony compounds and upon overall stability, a factor that influenced the low ratings for $XeF_2$ and $ClF_3O \cdot BF_3$.

The total ratings, based on a maximum value of 100, ranged from 28 to 79. With the uncertainties inherent in such ratings, the first seven reactants can be considered essentially equivalent in value.

TABLE 5. REACTANT RATING AND RANKING

| Reactant Composition | Ranking Criteria: Fluorine Content (25) | Availability, Cost (20) | Stability, Safety (35) | Product Contamination (15) | Ignition, Combustion (5) | Total Rating (100) |
|---|---|---|---|---|---|---|
| $KBrF_6$ | 20 | 19 | 25 | 10 | 5 | 79 |
| $KClF_4$ | 15 | 20 | 25 | 10 | 5 | 75 |
| $NOBrF_4$ | 18 | 20 | 20 | 10 | 3 | 71 |
| $RbBrF_6$ | 14 | 17 | 25 | 10 | 5 | 71 |
| $CsBrF_6$ | 10 | 17 | 25 | 10 | 5 | 67 |
| $(NO)_2MnF_6$ | 10 | 17 | 20 | 12 | 5 | 64 |
| $NF_4SbF_6$ | 14 | 16 | 15 | 8 | 5 | 58 |
| $ClF_3O \cdot BF_3$ | 11 | 12 | 12 | 10 | 3 | 48 |
| $NF_3O \cdot SbF_5$ | 4 | 9 | 15 | 8 | 3 | 39 |
| $XeF_2$ | 7 | 2 | 6 | 8 | 5 | 28 |
| $NF_4BF_4$ | 25 | (1) | 25 | 10 | 5 | 66 |
| $LiMnF_5$ | (1) | 20 | 25 | 15 | 5 | 66 |

Theoretical Analysis of Reactant Systems

In addition to the theoretical equilibrium calculations performed for each reactant to determine the degree of dissociation at fixed temperature levels (which provided the input for table A-1 in appendix A), theoretical equilibrium calculations were also performed for reactant systems combining the candidate reactants with various fuels. These calculations yielded the theoretical flame temperature and combustion product composition as a function of formulation composition, thereby providing a convenient means of comparing the potential of the candidates. It must be recognized, of course, that these calculations are only as valid as the thermodynamic data available. For those candidates that reached this stage of evaluation, only those systems containing manganese suffered from a relatively high uncertainty owing to the lack of current data for manganese species. All others are covered by the JANNAF Thermochemical Data Tables.

The results of these calculations are summarized in table 6 which tabulates the weight percent fluorine available as F, $F_2$, or $NF_3$. The reactant candidates were all evaluated initially with two fuels, $Si_3N_4$ and $Mg_3N_2$. The fluorine yield from all reagents except $(NO)_2MnF_6$ was found to be equal to or greater than 10 percent by weight with either one or both fuels. This result led to the early elimination of $(NO)_2MnF_6$ as a viable candidate.

The question of the degree of degradation of fluorine yield as the result of the use of polytetrafluoroethylene as a combination fuel and binder led to the next series of calculations. Here it was found that all of the reactant candidates except $KClF_4$ and $LiMnF_5$ experienced considerable reduction in fluorine yield. $KClF_4$ and $LiMnF_5$, even with the reduction in yield, met or essentially met the goal of 10 percent fluorine by weight. In these instances, the fluorocarbon could be effectively used as a processing aid in the formulation of gas generator grains.

The effect of incomplete conversion in the preparation of reactants $KBrF_6$ and $KClF_4$ on the resultant fluorine yield was evaluated. This evaluation was made because early literature references showed incomplete conversions to the products with some unconverted KF present. However,

TABLE 6. MAXIMUM CALCULATED FLUORINE YIELD COMPOSITIONS

| System No. | Reactant | Reactant Weight Percent | Fuel | Fuel Weight Percent | Flame Temperature, (K) | Weight Percent Fluorine (F, $F_2$, $NF_3$) |
|---|---|---|---|---|---|---|
| 2311 | $(NO)_2MnF_6$ | 93.00 | $Si_3N_4$ | 7.00 | 1177 | 5.41 |
| 2314 | $NOBrF_4$ | 90.00 | $Si_3N_4$ | 10.00 | 1588 | 9.91 |
| 2316 | $KBrF_6$ | 89.00 | $Si_3N_4$ | 11.00 | 1629 | 10.50 |
| 2317 | $KClF_4$ | 94.00 | $Si_3N_4$ | 6.00 | 1126 | 13.67 |
| 2321 | $LiMnF_5$ | 95.00 | $Si_3N_4$ | 5.00 | 1395 | 3.34 |
| 2325 | $(NO)_2MnF_6$ | 91.00 | $Mg_3N_2$ | 9.00 | 1350 | 8.77 |
| 2324 | $NOBrF_4$ | 88.00 | $Mg_3N_2$ | 12.00 | 1700 | 12.70 |
| 2326 | $KBrF_6$ | 88.00 | $Mg_3N_2$ | 12.00 | 1605 | 13.51 |
| 2327 | $KClF_4$ | 94.00 | $Mg_3N_2$ | 6.00 | 1101 | 16.44 |
| 2372 | $LiMnF_5$ | 99.00 | $Mg_3N_2$ | 1.00 | 921 | 10.86 |
| 2344 | $KMnF_5$ | 99.00 | $Mg_3N_2$ | 1.00 | 483 | 8.82 |
| 2343 | $KBrF_6$-KF (95/5) | 88.00 | $Mg_3N_2$ | 12.00 | 1629 | 12.60 |
| 2342 | $KClF_4$-KF (95/5) | 95.00 | $Mg_3N_2$ | 5.00 | 980 | 15.42 |
| 2335 | $(NO)_2MnF_6$ | 80.00 | $(C_2F_4)_n$ | 20.00 | 1251 | 2.28 |
| 2018 | $NOBrF_4$ | 75.00 | $(C_2F_4)_n$ | 25.00 | 1622 | 3.80 |
| 2334 | $KBrF_6$ | 75.00 | $(C_2F_4)_n$ | 25.00 | 1521 | 4.51 |
| 2333 | $KClF_4$ | 75.00 | $(C_2F_4)_n$ | 25.00 | 1040 | 9.49 |
| 2336 | $LiMnF_5$ | 99.00 | $(C_2F_4)_n$ | 1.00 | 752 | 11.23 |
| 2349 | $KClF_4$ | 88.00 | $NaN_3$ | 12.00 | 877 | 16.62 |
| 2350 | $LiMnF_5$ | 99.00 | $NaN_3$ | 1.00 | 791 | 11.70 |
| 2354 | $KClF_4$ | 95.00 | AlN | 5.00 | 1024 | 15.93 |
| 2355 | $LiMnF_5$ | 99.00 | AlN | 1.00 | 930 | 10.60 |
| 2359 | $KClF_4$ | 97.00 | Al | 3.00 | 1104 | 17.56 |
| 2361 | $LiMnF_5$ | 99.00 | Al | 1.00 | 1079 | 9.87 |
| 2385 | $LiMnF_5$ | 99.00 | Mg | 1.00 | 1030 | 10.42 |

current experience had led to the conclusion that conversions of 95 percent or higher could be expected under carefully conducted synthesis conditions. The theoretical calculations were therefore conducted with the appropriate level of KF contaminant. The calculated fluorine yield exhibited an almost linear dependence on contamination level in this range with approximately a 5 percent reduction in fluorine yield.

An alternative pentafluoromanganate salt, $KMnF_5$, was also evaluated with $Mg_3N_2$. As anticipated, the increase in formula weight resulting from the replacement of lithium by potassium reduced the fluorine yield proportionately. Consequently, this reactant was not considered further.

Both $LiMnF_5$ and $ClF_4$ were evaluated using $NaN_3$, AlN, and Al as common fuels. In all cases, the goal of 10 percent fluorine by weight was met or essentially met with considerably better yield derived from $ClF_4$. $LiMnF_5$ was evaluated with magnesium in addition and met the minimum goal requirement. The compositions giving the highest fluorine yield with $LiMnF_5$ in these instances fell in the very low fuel range, approximately 1 percent or lower.

The more complete summaries of the theoretical calculations from which table 6 was digested are collected in appendix B. These tables list, in addition to the parameters already specified, the concentrations of all products of any consequence, both condensed and gaseous.

Based on the foregoing analysis of candidate reactants and reactant systems, a series of five reactants were selected for experimental evaluation in the task 2 efforts. These compounds, listed in the order presented in task 2, are: $NOBrF_4$, $(NO)_2MnF_6$, $KBrF_6$, $ClF_4$, and $LiMnF_5$. With the exception of the last reactant, the other compounds met all criteria discussed previously based on information available at the time of selection. As discussed in the conclusion section of this report, the influence of contaminating species significantly altered the acceptability of these reactants.

$LiMnF_5$ was included as a candidate because it represented the only reactant that could provide essentially pure fluorine upon decomposition. This factor was deemed sufficiently important to permit relaxation of the available fluorine content restraint for this reactant.

## TASK 2: CHARACTERIZATION AND TESTING OF SELECTED CANDIDATE REACTANT SYSTEMS

The objective of this task was to evaluate the stability, ignitability, combustion, and exhaust properties of the candidate reactant systems selected on the basis of the task 1 efforts.

The experimental work performed toward achieving this objective was conducted in five successive stages: (1) synthesis of the candidate reactant in quantities sufficient for subsequent evaluations; (2) testing and rating of a broad spectrum of reactant-fuel systems for exothermic reactivity at elevated temperatures; (3) evaluating the compatibility and sensitivity of the reactants with fuels selected to introduce the least possible amount of contaminating gas products; (4) performing small-scale atmospheric pressure ignition and combustion tests on the reactant-fuel systems; and (5) pressing gas generator grains and evaluating their combustion in a motor at elevated pressures to determine pressure-burning rate data and flame temperature, and to analyze the gaseous combustion products to establish the extent of generation of fluorine gas.

The experimental procedures used throughout task 2 investigations were essentially equivalent for each of the candidate reactants. Consequently, these procedures are described in the section which follows and the experimental results achieved using these various procedures are subsequently set forth individually for each of the five selected reactants.

### Experimental Procedures

All of the fluorine compounds used for synthesis of the reactants and most of the fuels employed in this program were obtained from two sources, Ozark-Mahoning Company and Alfa-Ventron Company. The chemicals were used as-received and opened only in the dry box or to a vacuum system.

All fluorine reactant syntheses were conducted employing the all-metal vacuum system illustrated in figure 1. Two nickel reactors of 150-ml capacity and one stainless steel reactor of 60-ml capacity were used for the synthesis work. The specific synthesis procedures employed for each reactant synthesized are described in the sections devoted to the results obtained with the reactants.

Wet chemical analyses on fluorine-containing oxidizers were made in part by Galbraith Laboratories, Inc. of Knoxvile, Tenn. X-ray (Debye-Sherrer powder pattern) analyses were made by Analex of Palo Alto, CA., and nuclear activation analyses were made by General Activation Analysis, Inc. of San Diego, CA. Mass spectrographic analysis on gas products was made by Ultrachem Corporation of Walnut Creek, CA.

Since all of the fluorinated reactants and some of the fuels employed in this program were sensitive to decomposition by moisture to some degree, they were handled entirely in an inert atmosphere of dry nitrogen. A "Dri-Lab" inert atmosphere chamber, manufactured by D. L. Herring Corporation, was employed for practically all transfer operations.

Differential thermal analysis tests (DTA) were made using 10- to 15-mg samples of the dry gas generator mixtures under a nitrogen atmosphere in a 0.9-in.-diameter by 1.5-in.-long aluminum block heated by an 80-watt ITT Vulcan heating probe which produced a heating rate of 30 to 40 C/min. The absolute values and differential temperatures were recorded using a two-pen strip chart recorder. From analysis of the charts, the relative values of the autoignition temperatures and the magnitude of the associated exothermic energies were determined. In addition, the presence of endothermic melting occurring before attaining the autoignition temperature could be detected. Due to the reactive nature of the fluorinated reactants employed, the samples were tested in both glass and stainless steel sample tubes to eliminate any possible oxidizer-glass exotherms.

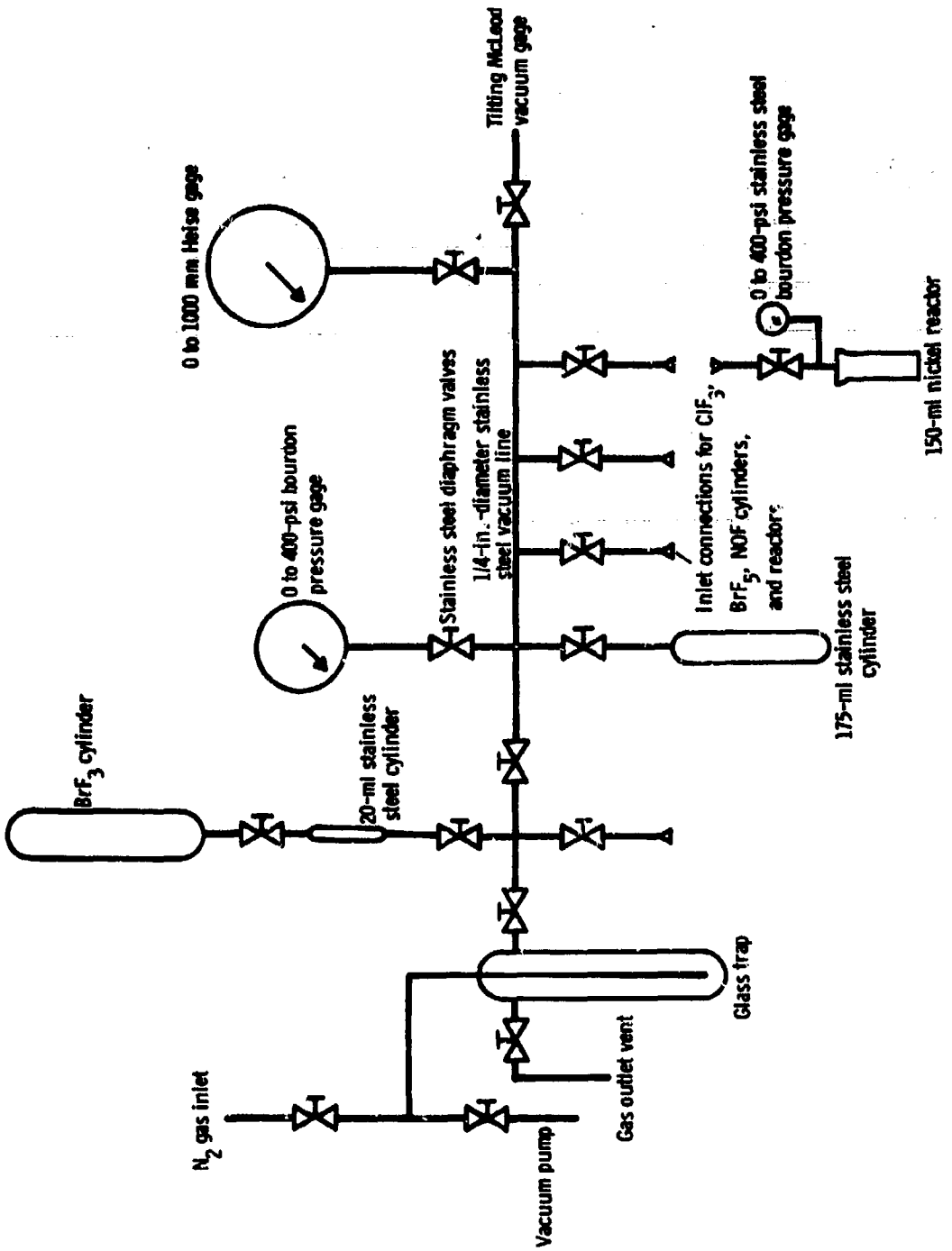


Figure 1. All-Metal Vacuum System

A large number of reactant systems was screened with atmospheric pressure combustion studies. The nitrogen atmosphere ignition and combustion testing apparatus used is shown in figure 2. It is essentially an all-glass system to allow for visual observations of the ignition and burning processes. A stainless steel grain case was used only in cases where flame temperatures and atmospheric burning rates were being measured. Chromel-alumel thermocouples attached to a 5-124 CEC recording oscillograph were used to obtain flame temperatures and burning rates.

Impact and friction sensitivity tests were made on all reactant-fuel systems considered promising from the ignitability and combustion testing. The impact tests were conducted with an Olin-Mathieson-type drop weight tester. The samples employed in these tests were placed in sealed sample holders in a nitrogen atmosphere dry box to avoid hydrolytic reaction before or during the tests. The friction tests were conducted using an ESSO

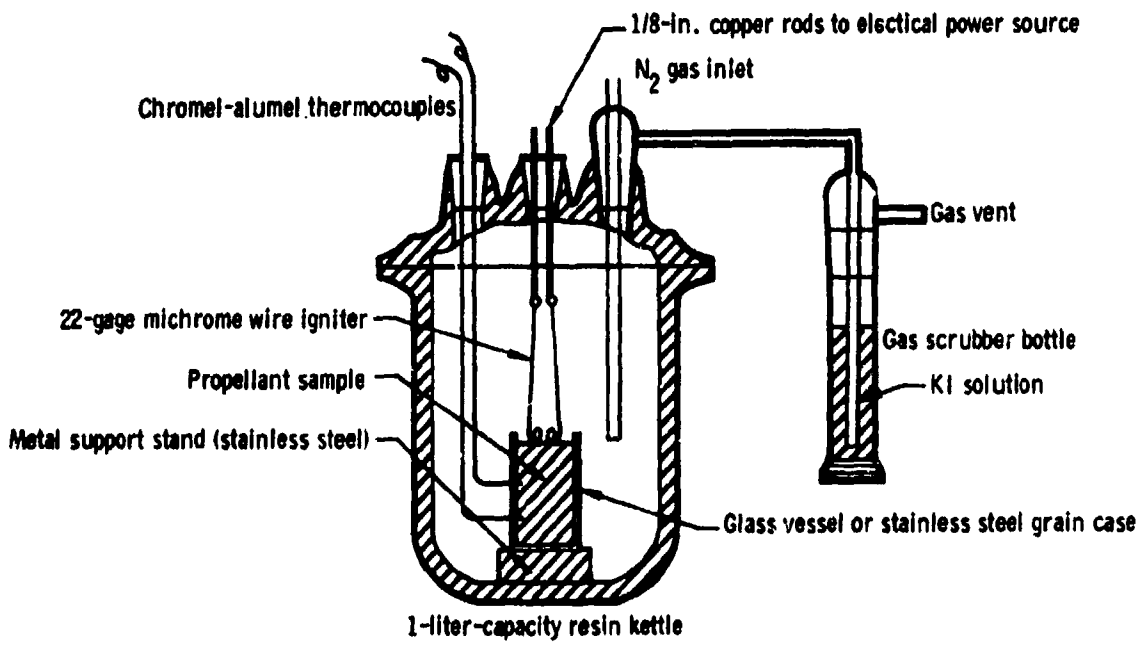


Figure 2. Ignition and Combustion Testing Apparatus

friction tester. The tester was placed in a large plastic bag and flushed with nitrogen until the relative humidity was below 10 percent before starting testing. The samples were mixed with diamond grit and a maximum of 70 ft-lb of work applied.

The most promising reactant system candidates for fluorine gas generators were selected for small motor testing based on the atmospheric ignition and combustion screening tests described above. The formulations were mixed and fabricated into grains for test firing in a small test motor. The grain cases were constructed of stainless steel tubing 1.92 in. long having an internal diameter of 0.9 in. Four pressings of equal amounts of the thoroughly mixed dry reactant-fuel composition were made per grain. A force of 2000 lb (3000 psi) was applied with each pressing using a stainless steel punch and an RC-55 Enerpac 5-ton hydraulic cylinder. The entire operation was conducted in a dry box under constant nitrogen flush. The small test motor assembly is shown in figures 3 and 4. The material of construction was stainless steel with Teflon O-ring seals. The assembly consisted of tie rods, transducer and thermocouple attachment tee, solid spacer, grain case, end closures (with a nichrome wire igniter sealed through one end closure), motor body, and steel nozzle and holder attachment. The pressures developed in the motor were determined with a 0- to 1000-psia-range Statham transducer, to which was attached a 1000-psig rupture disc assembly. The transducer was attached to a 5-124 CEC recording oscillograph operated at a chart speed of .25 in./sec. The chamber pressure was varied from 14.7 to 500 psia by variations in the nozzle diameter. The exhaust line from the motor was provided with gas sampling takeoff and vacuum.

Experimental Results

For the task 2 evaluation, the five reactants selected from the task 1 studies were (1) nitrosonium tetrafluorobromate, $NOBrF_4$; (2) nitrosonium hexafluoromanganate, $(NO)_2MnF_6$; (3) potassium hexafluorobromate, $KBrF_6$; (4) potassium tetrafluorochlorate, $KClF_4$; and (5) lithium pentafluoromanganate, $LiMnF_5$. The synthesis, DTA, ignition and combustion studies, hazard evaluation, and small motor test results are consolidated for each reactant in the subsections which follow.

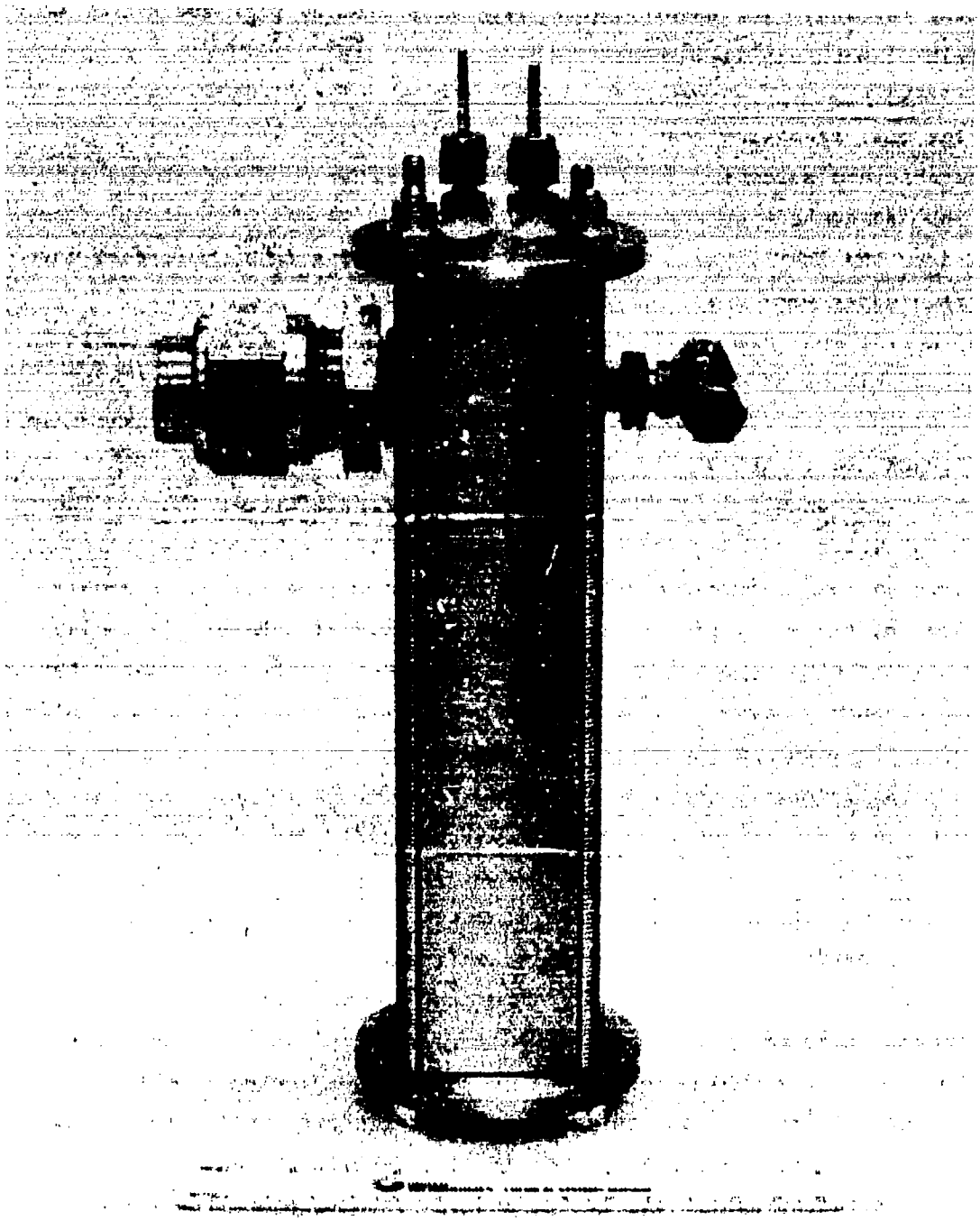

Figure 3. Small Test Motor

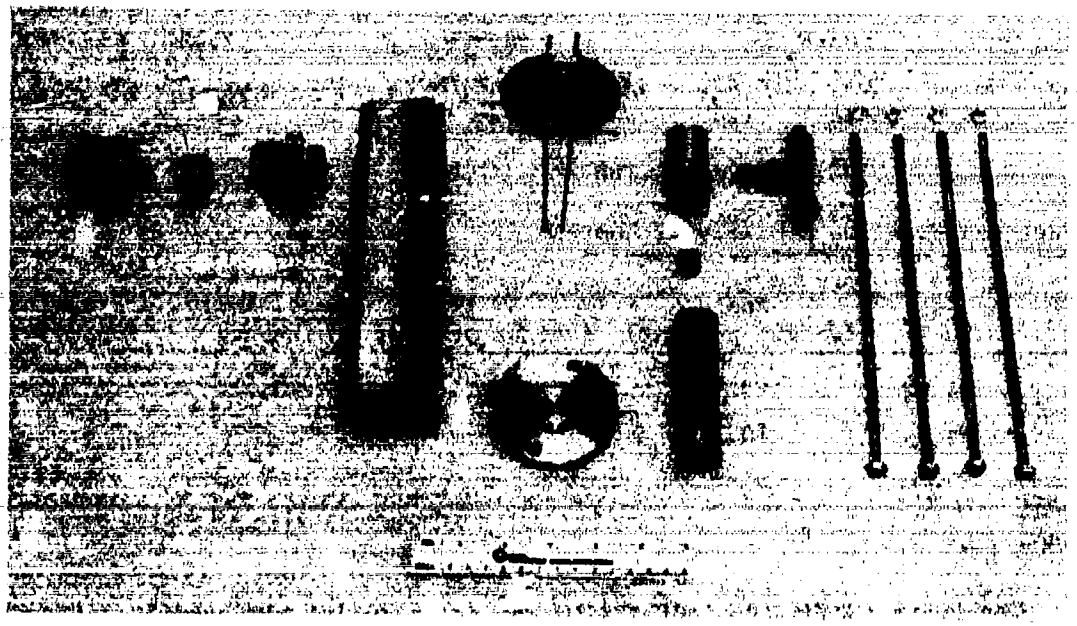

Figure 4. Small Test Motor - Exploded View

Nitrosonium Tetrafluorobromate - The compound $NOBrF_4$ is well-characterized and exhibits adequate stability as a reactant for a fluorine gas generator. The reactant is easily synthesized pure by condensation of NOF with $BrF_3$[24], both of these precursors being readily available. For this program, this synthesis method was employed. Bromine trifluoride was placed in a nickel reactor by a vacuum-gravity technique and a slight stoichiometric excess of NOF was added by vacuum distillation. A total of 32.3 g of $NOBrF_4$ was prepared with a 96.6 percent conversion as shown in table 7. DTA tests showed that $NOBrF_4$ decomposed at 180 C with a large endothermic heat of dissociation.

During preparation of candidate reactant systems for DTA tests, spontaneous ignition occurred upon mixing $NOBrF_4$ with B, $Si_3N_4$, S, or BN. On the other hand, tetrafluoroethylene, $Mg_3N_2$, Kel-F, Al, Mg, and $NaN_3$ were suitably compatible to permit mixing and DTA results were obtained as shown in table 8. The $NaN_3/NOBrF_4$ composition gave an exothermic reaction at 102 C, which is considered marginal for a safe gas generator system.

TABLE 7. PREPARATION AND PROPERTIES OF $NOBrF_4$ REACTANT SYSTEMS

Preparation of $NOBrF_4$

| Prep. No. | NOF, (g) | NOF, (moles) | $BrF_3$, (g) | $BrF_3$, (moles) | $BrF_3$/NOF, (mole ratio) | Reaction Temp. (C) | Conversion, (percent) |
|---|---|---|---|---|---|---|---|
| 1 | 8.986 | .183 | 24.667 | .180 | .984 | 20 | 96.6 |

Impact and Friction Sensitivity Tests of $NOBrF_4$ and $Mg_3N_2$

| Test No. | Fuel | Fuel, (weight percent) | $NOBrF_4$, (weight percent) | Impact Sensitivity, (kg-cm) | Friction Sensitivity[a] |
|---|---|---|---|---|---|
| 1 | $Mg_3N_2$ | 13.5 | 86.5 | 7.6 | - |
| 2 | $Mg_3N_2$ | 10.1 | 89.9 | - | no sensitivity |

[a]Diamond grit at 70 ft-lb.

The $NOBrF_4/Mg_3N_2$ reactant system was selected for atmospheric pressure ignition-combustion testing. Ignition was observed to occur readily with an 87 weight percent $NOBrF_4$ composition, combustion was complete, and the burning rate was moderate in a tamped powder configuration. Impact and friction tests were made on this composition; the mixture was found to be very impact-sensitive but not friction-sensitive, as shown in table 7.

Work on $NOBrF_4$ was not continued in light of the potential detrimental effects of BrF and NOF on deactivation and the high reactivity of $NOBrF_4$ with fuels observed during the early exploratory tests described above.

Nitrosonium Hexafluoromanganate - The compound $(NO)_2MnF_6$ has been reported to have sufficient stability to be considered as a reactant for fluorine gas generation. For preliminary screening studies, the compound was synthesized by the procedure of Bouy[20] by reaction of $MnF_3$ and NOF in a large excess of $BrF_3$ at 100 C. The excess $BrF_3$ was subsequently removed at 120 to 150 C. The conversion, noted as slightly greater than 100 percent, was probably a result of the presence of $NOBrF_4$ produced from a slight stoichiometric excess of NOF introduced into the reactor. DTA of the $(NO)_2MnF_6$ reaction product

TABLE 8. DTA OF $NOBrF_4$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $NOBrF_4$, (weight percent) | Endotherms, (C) | Exotherms, (C) |
|---|---|---|---|---|---|
| 1 | None | - | 100 | 179s | |
| 2 | $(C_2F_4)n$ | 9.9 | 90.1 | 190s | |
| 3 | B | - | - | Spontaneous ignition on mixing | |
| 4 | $Si_3N_4$ | 10.7 | 89.3 | 200m<br>Sporadic ignition on mixing | 83s |
| 5 | $Mg_3N_2$ | 24.5 | 75.5 | 176s | |
| 6 | Kel-F | 10.6 | 89.4 | 179s | |
| 7 | S | - | - | Spontaneous ignition on mixing | |
| 8 | Al | 10.1 | 89.9 | 179s | |
| 9 | Mg | 10.6 | 89.4 | 171s | |
| 10 | $NaN_3$ | 10.6 | 89.4 | 157m-w | 102s |
| 11 | BN | - | - | Gas evolution on mixing | |

NOTE: s = strong, m = medium, w = weak

showed no tendency for decomposition below 200 C (see table 9). These data thereby confirm the reported stability of the compound.

Mixtures of $(NO)_2MnF_6$ and selected fuels were made to provide preliminary DTA data. As shown in table 9, the material was found to be compatible with every fuel tested, including fuels that resulted in spontaneous ignition with $NOBrF_4$. DTA results showed most fuels with $(NO)_2MnF_6$ gave only endotherms at temperatures of 200 C or below (e.g.,

TABLE 9. DTA OF $(NO)_2MnF_6$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $(NO)_2MnF_6$, (weight percent) | Endotherms, (C) | Exotherms, (C) |
|---|---|---|---|---|---|
| 1 | None | - | 100.0 | 200vw, 303w | 290vw |
| 2 | $(C_2F_4)n$ | 9.0 | 91.0 | 200w, 300wm | 284w |
| 3 | Al | 8.8 | 91.2 | 200w, 300wm | 254w, 287w |
| 4 | B | 9.7 | 90.3 | - | 97wm, 138vs |
| 5 | Mg | 10.5 | 89.5 | 200w, 298m | 287w |
| 6 | S | 10.1 | 89.9 | 195w, 271m | - |
| 7 | $NaN_3$ | 11.2 | 88.8 | - | 127s |
| 8 | $Mg_3N_2$ | 9.8 | 90.2 | 200w, 300m | 287vw |

NOTE: vs = very strong, s = strong, m = moderate, w = weak, vw = very weak

perfluoroethylene, aluminum, sulfur, and magnesium nitride). Exotherms at comparatively low temperatures were observed with boron (100 C) and $NaN_3$ (127 C); magnesium showed a higher exotherm at 287 C.

Because of the reduced fluorine levels calculated for reactant systems employing $(NO)_2MnF_6$, no further work was conducted with $(NO)_2MnF_6$.

Potassium Hexafluorobromate - The compound $KBrF_6$ has previously been shown to be a thermally stable material exhibiting high reactivity characteristics with fuels.

For this work, $KBrF_6$ was prepared from KF and $BrF_5$ according to the procedure described by MacLaren et al.[21] An excess of $BrF_5$ was vacuum distilled onto KF in a nickel reactor and this mixture was heated to 100 C for several hours. The unreacted $BrF_5$ was subsequently removed by vacuum

distillation. Five preparations of $KBrF_6$ were made as shown in table 10. As previously reported, it was found that the conversion to $KBrF_6$ was about 80 percent and independent of the reaction time and amount of excess $BrF_5$. To improve the conversion of KF to $KBrF_6$, the reaction product from preparation 5 was removed from the reactor, pulverized, and returned to the reactor with additional $BrF_5$. The conversion increased from the 80 percent level to approximately 95 percent by this treatment.

$KBrF_6$ is thermally stable to about 200 C as shown by the DTA results in table 11. With fuels, however, the compound was found to react at much lower temperatures. As with $NOBrF_4$, $KBrF_6$ reacted spontaneously when mixed with boron. With $Si_3N_4$ and $SiO_2$, exotherms were measured at temperatures of 130 to 160 C. No exotherms to the maximum experimental temperature of 500 C were observed with perfluoroethylene or $Mg_3N_2$.

Impact and friction tests were made on a 92 weight percent $KBrF_6$/8 weight percent $Mg_3N_2$ composition and the impact sensitivity was measured to be 15 kg-cm with no measurable friction sensitivity. These results indicate that $KBrF_6$ systems are safer to handle than the equivalent $NOBrF_4$ systems.

An atmospheric pressure ignition and combustion test was conducted with a tamped mixture of 89.6 weight percent $KBrF_6$ and 10.4 weight percent $Mg_3N_2$. Ignition occurred readily, and the composition burned completely with a low burning rate.

A total of five grains of between 16 and 24 g each with the approximate composition of 90 weight percent $KBrF_6$/10 weight percent $Mg_3N_2$ were prepared by pressing at a nominal pressure of 3000 psi giving an average grain density of 2.21 g/cc. The test data obtained from these grains are summarized in table 12. One grain was fired in the atmospheric pressure test apparatus and the other four were tested in the small test motor. The flame temperature measured by a thermocouple in the test grain at 1 atm varied from 1143 to 1403 K. Plugging of the motor nozzle with melted and resolidified igniter wire particles was a problem in two of the tests. This problem was overcome by employing an oversized nozzle and maintaining a constant nitrogen flow to

TABLE 10. PREPARATION OF $KBrF_6$

| Prep. No. | KF, (g) | KF, (moles) | $BrF_5$, (g) | $BrF_5$, (moles) | $BrF_5$/KF, (mole ratio) | Reaction Temp., (C) | Conversion, (percent) |
|---|---|---|---|---|---|---|---|
| 1 | 4.832 | .0832 | 20.55 | .117 | 1.41 | 100 | 71.5 |
| 2 | 20.945 | .360 | 105.7 | .604 | 1.68 | 135 | 84.5 |
| 3 | 19.460 | .335 | 105.4 | .603 | 1.80 | 135 | 82.1 |
| 4 | 28.088 | .483 | 101.4 | .580 | 1.20 | 135 | 81.5 |
| 5 | 25.297 | .435 | 103.6 | .592 | 1.36 | 135 | 79.4 |
| 6 | a | (75.710g) | 58.7 | .336 | - | 135 | 94.5 |

[a] Product from reaction No. 5.

TABLE 11. DTA OF $KBrF_6$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $KBrF_6$, (weight percent) | Endotherms, (C) | Exotherms, (C) |
|---|---|---|---|---|---|
| 1 | - | - | 100 | 190w, 292w | - |
| 2 | $(C_2F_4)n$ | 9.5 | 90.5 | 190w, 292w | - |
| 3 | B | - | - | Spontaneous ignition on mixing | |
| 4 | $Si_3N_4$ | 9.6 | 90.4 | - | 130 vs (flame) |
| 5 | $Mg_3N_2$ | 12.5 | 87.5 | 184vw, 279vw | - |
| 6 | $SiO_2$ | 10.3 | 89.7 | - | 161m |
| 7 | $Si_3N_4$ | 5.0 | 95.0 | - | 135s |
| 8 | $Si_3N_4$ | 1.0 | 99.0 | 186vw, 287vs | - |

NOTE: vs = very strong, s = strong, m = medium, w = weak, vw = very weak

TABLE 12. GRAIN COMBUSTION TESTS OF $KBrF_6$ AND $Mg_3N_2$

| Test No. | Fuel | Fuel Weight Percent | $KBrF_6$, (weight percent) | Grain Weight, (g) | Grain Length, (in.) | Grain Density, (g/cc) | Burning Rate, (in./sec) |
|---|---|---|---|---|---|---|---|
| 1 | $Mg_3N_2$ | 10.2 | 89.8 | 16.637 | .74 | 2.16 | .03 |
| | Test pressure: 14.7 psia - combustion complete - some liquefaction during combustion | | | | | | |
| 2 | $Mg_2N_3$ | 9.5 | 90.5 | 22.467 | .99 | 2.19 | - |
| | Combustion complete - no pressure measurement- residue: 64.6% | | | | | | |
| 3 | $Mg_3N_2$ | 10.0 | 90.0 | 21.967 | .95 | 2.23 | - |
| | Ignition spike - 1000-psi rupture disk relieved | | | | | | |
| 4 | $Mg_3N_2$ | 9.6 | 90.4 | 23.737 | 1.02 | 2.24 | - |
| | Melted ignition wire plugged nozzle - 1000-psi rupture disk relieved | | | | | | |
| 5 | $Mg_3N_2$ | 10.4 | 89.6 | 23.694 | 1.01 | 2.25 | .05 |
| | Nitrogen flow permitted use of oversize nozzle - $N_2$ pressure: 63-psia- $F_2$ pressure: 127-psia max. | | | | | | |

provide a pressure level in the motor before and during combustion. Measured burning rates were comparatively low, .03 in./sec at 14.7 psia and .05 in./sec at approximately 100 psia.

From these tests, it appeared that this solid reactant system could be successfully developed. However, efforts on the $KBrF_6$ system were discontinued during the task 2 portion of the program because of the uncertainties of the influence of the combustion product, BrF, on laser performance.

Potassium Tetrafluorochlorate - The preparation and identification of $KClF_4$ has been reported; however, information on the physical and chemical properties of this compound is limited.

For the investigations in this program, $KClF_4$ was prepared from KF and

$ClF_3$ according to the procedure described by MacLaren et al.[21] A series of eight syntheses was conducted to prepare sufficient material for test evaluation. The experimental conditions are given in table 13. A total of 547 g was prepared with purities ranging from 92.8 to 98.5 percent. The lowest conversion was obtained in preparation No. 2, whereby a stoichiometric quantity of $ClF_3$ was added to the KF. In all other preparations, excess $ClF_3$ was used and subsequently removed by vacuum distillation.

DTA tests of $KClF_4$ showed some endothermic activity at 97 to 100 C which is most likely melting. The higher endotherms at 230 to 240 C are consistent with the decomposition temperature reported in the literature.

An extensive number of fuels with $KClF_4$ were examined by DTA, as shown in table 14. With boron, $Li_3N$, and $Ca_3N_2$, ignition between $KClF_4$ and the fuels occurred on mixing. Low temperature exotherms were observed with sulfur, BN, and $NaN_3$. Of the nitrides, only $Mg_3N_2$ showed stability above 200 C. Compared to the previous reactants, the reactivity of $KClF_4$ appeared less than either $NOBrF_4$ or $KBrF_6$.

An atmospheric pressure ignition and combustion test was made with an 88.5 weight percent $KClF_4$/11.5 weight percent $Mg_3N_2$ mixture. Incomplete combustion was obtained with the tamped powder which might be expected from the weak exothermic reactivity recorded by DTA. On the other hand, a tamped mixture of 89.9 weight percent $KClF_4$/10.1 weight percent $NaN_3$ ignited easily, had a reasonable burning rate, and burned completely.

The impact and friction sensitivities of $KClF_4$ with the most promising fuels were evaluated and the results are listed in table 15. The candidate $KClF_4$ reactant systems are all safe to handle according to these results if the proper precautions are taken. The impact sensitivities for the reactants appear to correlate with their reactivity with the fuels in that the impact sensitivities decrease in the order: $NOBrF_6 > KBrF_6 > KClF_4$.

A total of 16 pressed grains were prepared from various compositions of $KClF_4$ and fuels using a compaction pressure of 3000 psi. One grain, prepared

TABLE 13. PREPARATION OF $KClF_4$

| Prep. No. | KF, (g) | KF, (moles) | $ClF_3$, (g) | $ClF_3$, (moles) | $ClF_3$/KF, (mole ratio) | Reaction Temp., (C) | Conversion, (percent) |
|---|---|---|---|---|---|---|---|
| 1 | 9.199 | .158 | 33.9 | .367 | 2.32 | 130 | 97.7 |
| 2 | 16.945 | .292 | 27.0 | .292 | 1.00 | 135 | 92.8 |
| 3 | 21.921 | .377 | 49.5 | .535 | 1.42 | 135 | 96.4 |
| 4 | 23.634 | .407 | 48.4 | .523 | 1.29 | 135 | 96.7 |
| 5 | 27.056 | [illegible] | 111.8 | 1.209 | 2.59 | 135 | 97.1 |
| 6 | 26.477 | .456 | 98.1 | 1.061 | 2.33 | 135 | 94.0 |
| 7 | 28.372 | .488 | 84.3 | .912 | 1.87 | 135 | 97.4 |
| 8 | 24.806 | .427 | 94.4 | 1.021 | 2.39 | 135 | 98.5 |

using $Mg_3N_2$ as the fuel, was tested at atmospheric pressure and did not sustain combustion. All other grains were tested in the small test motor. Five $KClF_4$-$NaN_3$ grains were prepared; however, during the preparation of three other $KClF_4$-$NaN_3$ grains, spontaneous ignitions occurred during either the mixing or pressing operations. All five $KClF_4$-$NaN_3$ grains fired in the motor ignited and burned successfully. Test data are noted in table 16 as tests 3 through 7. Burning rates varied from .05 to .09 in./sec. The $KClF_4$-$NaN_3$ grain used in test No. 8 was fired into an evacuated holding cylinder for gas sampling. The burning rate was very low and the limited quantity of gas evolved in comparison to the other tests showed the influence of a large pressure effect. A sample of the combustion products was submitted for mass spectrometer analysis; however, instrumental difficulties prevented a satisfactory analysis.

A total of seven additional grains were prepared from the $KClF_4$-Al reactant system using aluminum powder of 6 to 9 microns. The first grain had a 95 weight percent $KClF_4$/5 weight percent Al composition and was successfully fired in the motor (test No. 10). The burning rate at a chamber

TABLE 14. DTA OF $KClF_4$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $KClF_4$, (weight percent) | Endotherms, (C) | Exotherms, (C) |
|---|---|---|---|---|---|
| 1 | - | - | 100.0 | 100w, 236w, 265w | - |
| 2 | $(C_2F_4)n$ | 10.1 | 89.9 | 100w, 233w, 260w | - |
| 3 | $Si_3N_4$ | 9.6 | 90.4 | 97w | 149vs |
| 4 | BN | 16.8 | 83.2 | - | 100w, 119s |
| 5 | B | - | - | Spontaneous ignition on mixing | |
| 6 | $Mg_3N_2$ | 22.2 | 77.8 | 97w, 239w, 260w | 285w |
| 7 | Al | 10.0 | 90.0 | 97w | 281s |
| 8 | Mg | 9.9 | 90.1 | 97w, 238w, 265w | 260w |
| 9 | S | 9.7 | 90.3 | - | 94vs |
| 10 | $NaN_3$ | 10.1 | 89.9 | - | 105s |
| 11 | Kel-F | 10.3 | 89.7 | 97w, 233w, 287w | 300w |
| 12 | $Li_3N$ | - | - | Spontaneous ignition on mixing | |
| 13 | $Ca_3N_2$ | - | - | Spontaneous ignition on mixing | |
| 14 | AlN | 5.1 | 94.9 | 101w, 240w, 289w | 168m |

NOTE: vs = very strong, s = strong, m = medium, w = weak

pressure of approximately 300 psia was .04 in./sec. The high theoretical flame temperature of 1700 C and the presence of corrosive gases combined to cause partial consumption of the stainless steel grain case. Five attempts were made to successfully burn grains prepared with a lower aluminum content of 97 weight percent $KClF_4$/3 weight percent Al. The first grain could not be ignited even after prolonged heating with a nichrome wire grid. To facilitate ignition, more easily ignited compositions were placed as a cap on top of the 97 weight percent $KClF_4$/3 weight percent Al grains. The first cap

TABLE 15. SENSITIVITY TEST DATA OF $KClF_4$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $KClF_4$, (weight percent) | Friction Sensitivity, (kg-cm) | Friction Sensitivity[a] |
|---|---|---|---|---|---|
| 1 | $Mg_3N_2$ | 11.5 | 88.5 | 36.5 | - |
| 2 | $Mg_3N_2$ | 10.1 | 89.9 | - | No sensitivity |
| 3 | $NaN_3$ | 10.1 | 89.9 | 16.0 | No sensitivity |
| 4 | Al | 5.4 | 94.6 | 54.0 | No sensitivity |
| 5 | AlN | 5.1 | 94.9 | 13.3 | No sensitivity |

[a] Diamond grit at 70 ft-lb.

employed was a 90 weight percent $KBrF_6$/10 weight percent $Mg_3N_2$ composition; this cap ignited satisfactorily but ignition of the grain did not occur (test No. 12). A cap of 95 weight percent $KClF_4$/5 weight percent Al was next examined and gave the same results. The cap residue was removed from the grain and a second cap of 90 weight percent $KClF_4$/10 weight percent $NaN_3$ successfully ignited the grain (test No. 13). This same composition cap was not successful in igniting a second grain (test No. 14), nor was a cap comprised of $AgF_2$-Mg.

A grain was formulated with 96 weight percent $KClF_4$, 3 weight percent Al, and 1 weight percent $NaN_3$. While it could not be ignited directly with the hot nichrome igniter grid, combustion was complete when capped with an 89 weight percent $KClF_4$/11 weight percent $NaN_3$ composition. A burning rate of .03 in./sec was measured at a chamber pressure of 30 to 80 psia.

Four grains were pressed and fired in the small motor with a 95 weight percent $KClF_4$/5 weight percent AlN composition. They all ignited easily and burned completely with burning rates ranging from .014 to .055 in./sec. One grain was fired into a holding cylinder, previously passivated with fluorine, which had been evacuated and filled to one atmosphere with helium. A sample of the combustion gas products was submitted for mass spectrographic

TABLE 16. COMBUSTION OF GRAINS OF $KClF_4$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $KClF_4$, (weight percent) | Grain Weight (g) | Grain Length, (in.) | Density, (g/cc) | Burning Rate, (in./sec) | Chamber Pressure, (psia) | Residue Weight (percent) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $Mg_3N_2$ | 6.2 | 93.8 | 9.93 | .57 | 1.67 | - | - | - |
| | Ignition and combustion occurred only in vicinity of igniter | | | | | | | | |
| 2 | $NaN_3$ | 11.0 | 89.0 | - | - | - | - | - | - |
| | Ignited on mixing | | | | | | | | |
| 3 | $NaN_3$ | 11.0 | 89.0 | 17.46 | .99 | 1.69 | .05 | 60[a] | 58.8 |
| 4 | $NaN_3$ | 11.0 | 89.0 | 17.74 | 1.01 | 1.68 | .05 | 80[a] | 67.0 |
| 5 | $NaN_3$ | 11.0 | 89.0 | 19.43 | 1.11 | 1.67 | - | - | - |
| | Spontaneous ignition of grain during motor loading operation | | | | | | | | |
| 6 | $NaN_3$ | 11.0 | 89.0 | 19.32 | 1.09 | 1.69 | .09 | 40 | 55.0 |
| 7 | $NaN_3$ | 11.0 | 89.0 | 18.05 | 1.03 | 1.68 | .05 | 35 | 55.1 |
| 8 | $NaN_3$ | 11.0 | 89.0 | 19.42 | 1.10 | 1.69 | - | 500mm | 68.3 |
| | Vacuum ignition, products collected for analysis | | | | | | | | |
| 9 | $NaN_3$ | 11.0 | 89.0 | - | - | - | - | - | - |
| | Ignited on mixing | | | | | | | | |
| 10 | Al | 5.0 | 95.0 | 18.56 | 1.01 | 1.76 | .04 | ~300 | - |
| | Nozzle plugging occurred, grain case wall burned | | | | | | | | |
| 11 | Al | 3.0 | 97.0 | 18.83 | 1.01 | 1.79 | - | - | - |
| | Grain did not ignite | | | | | | | | |

TABLE 16 (continued)

| Test No. | Fuel | Fuel Weight Percent | $KClF_4$, (weight percent) | Grain weight, (g) | Grain Length, (in.) | Density, (g/cc) | Burning Rate, (in./sec) | Chamber Pressure, (psia) | Residue Weight, (percent) |
|---|---|---|---|---|---|---|---|---|---|
| 12 | Al | 3.0 | 97.0 | 18.91 | 1.03 | 1.76 | - | - | - |
| | Igniter cap of 89.7 weight percent $KBrF_6$/10.3 weight percent $Mg_3N_2$ did not ignite grain | | | | | | | | |
| 13 | Al | 3.0 | 97.0 | 19.29 | 1.05 | 1.77 | .05 | ~50 | - |
| | Igniter cap of 95.0 weight percent $KClF_4$/5.0 weight percent Al did not ignite grain<br>Igniter cap of 90.0 weight percent $KClF_4$/10.0 weight percent $NaN_3$ ignited grain, successful combustion | | | | | | | | |
| 14 | Al | 3.0 | 97.0 | 20.15 | 1.08 | 1.77 | - | - | - |
| | Two separate igniter caps (90.0 weight percent $KClF_4$/10 weight percent $NaN_3$, 95.0 weight percent $AgF_2$/5.0 weight percent Mg) failed to ignite grain | | | | | | | | |
| 15 | Al<br>$NaN_3$ | 3.0<br>1.0 | 96.0 | 16.32 | .89 | 1.76 | .03 | ~50 | - |
| | Igniter cap of 88.9 weight percent $KClF_4$/11.1 weight percent $NaN_3$ required for ignition and combustion | | | | | | | | |
| 16 | AlN | 5.6 | 94.4 | 17.46 | .94 | 1.78 | .03 | ~400 | 81.1 |
| | Screen filters plugged | | | | | | | | |
| 17 | AlN | 4.9 | 95.1 | 20.65 | 1.13 | 1.76 | .014 | 50 | 48.4 |
| | Combustion complete with intermittent burning | | | | | | | | |
| 18 | AlN | 5.0 | 95.0 | 20.66 | 1.13 | 1.76 | .055 | 200 | 64.7 |
| 19 | AlN | 5.0 | 95.0 | 19.49 | 1.07 | 1.75 | .024 | ~15 | 52.8 |
| | Gas products collected for analysis | | | | | | | | |

[a] Nitrogen flow added to permit use of larger nozzles.

analysis. The analysis showed the major components of the sample to be ClF and $Cl_2$ accounting for over 90% of the sample. Minor components included $CH_2ClF$, $CH_2F_2$, $CHF_3$, and $F_2$. The $KClF_4$-AlN reactant system operated most successfully of the $KClF_4$ reactant systems.

Lithium Pentafluoromanganate - Very limited information was available from the literature on $LiMnF_5$. Hoppe, Dähne and Klemm[31] have reported preparing the compound by fluorinating $LiMnF_3$ at 450 to 500 C in a flow system with sublimation of $LiMnF_5$ and collection on a cold finger. Since this method is not considered practical for large-scale production, studies were performed under the IR&D program to define a more straightforward synthesis route to $LiMnF_5$. These studies applied the method for preparation of $KMnF_5$ of Sharpe and Woolf[30] to $LiMnF_5$.

A series of reactions was performed using variously $MnF_3$, $MnO_2$, or $MnCl_2$ as the starting material with LiF and $BrF_3$. A large excess of $BrF_3$, which acts both as a solvent and reactant, was used. From these experiments, it was determined that the reaction with $MnCl_2$ occurred readily at ambient temperature and the accompanying exotherm resulted in a significant temperature rise. Ten syntheses using $MnCl_2$ were conducted and are summarized in table 17. In each case, there was a pressure increase during reaction; percent conversion to $LiMnF_5$ on a weight basis was 95 to 100 percent. The gaseous products formed during the synthesis of $LiMnF_5$ (preparation No. 8), as analyzed by mass spectrometer, are shown in table 18.

The $Cl_2$, BrCl, and $Br_2$ are expected products. The source of the hydrogen is not known. The $MnCl_2$, used as a starting material, was investigated to ensure that it was not a hydrate. Chlorine by analysis was 54.73 percent (theoretical = 56.35 percent) and, upon vacuum drying at 155 C, only a 1.27 percent weight loss was found. A sample was also submitted for X-ray analysis and found to match the ASTM d-spacings for anhydrous $MnCl_2$. It was concluded that the hydrogen was obtained from secondary reactions during the mass spectrometer analysis.

TABLE 17. PREPARATION OF $LiMnF_5$ AND $MnF_4$

| Prep. No. | Mn Compound Halide | Mn Compound Halide, (moles) | LiF, (moles) | $BrF_3$, (moles) | $BrF_3$/Mn, (mole ratio) | Reaction Temperature, (C) | Conversion, (percent) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 1 | $MnCl_2$ | .0400 | .403 | .367 | 9.2 | 100 | 93.2 | Rust solids |
| 2 | $MnCl_2$ | .0719 | .0729 | .213 | 3.0 | 100 | 99.0 | Gold solids |
| 3 | $MnCl_2$ | .149 | .148 | .524 | 3.5 | 100 | (100.0) | Gold solids |
| 4 | $MnCl_2$ | .0899 | .906 | .330 | 3.7 | 100 | 94.9 | Gold solids |
| 5 | $MnCl_2$ | .101 | .102 | .455 | 4.5 | 100 | 93.8 | Gold solids |
| 6 | $MnCl_2$ | .0997 | .0976 | .348 | 3.5 | 100 | 97.5 | Gold solids |
| 7 | $MnCl_2$ | .2205 | .2182 | .5558 | 2.5 | 100 | (102.3) | Gold solids |
| 8 | $MnCl_2$ | .163 | .166 | .602 | 3.7 | 135 | 97.1 | Gold solids |
| 9 | $MnCl_2$ | .0588 | .0614 | .332 | 4.6 | 100 | 85.4 | Rust solids |
| 10 | $MnCl_2$ | .164 | .167 | .723 | 4.4 | 110 | 97.0 | Gold solids |
| 11 | $MnBr_2$ | .0637 | .0665 | .351 | 5.5 | 20 | (100.1) | Greenish-gold solids |
| 12 | $MnBr_2$ | .1358 | .1379 | .666 | 4.9 | 20 | 97.3 | Greenish-gold solids |
| 13 | $MnBr_2$ | .1393 | .1384 | .7194 | 5.2 | 20 | 92.9 | Greenish-gold and rose-red solids |

TABLE 17. (continued)

| Prep. No. | Mn Compound Halide | Mn Compound Halide, (moles) | LiF, (moles) | $BrF_3$, (moles) | $BrF_3$/Mn, (mole ratio) | Reaction Temperature, (C) | Conversion, (percent) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 14 | $MnCl_2$ | .028 | - | .35 | 12.7 | 110 | $MnF_4$ (113.2) | Purplish-blue solids |
| 15 | $MnBr_2$ | .0885 | - | .3496 | 3.95 | 20 | $MnF_4$ 96.2 | Purplish-blue solids |
| 16 | $MnF_2$ | .08998 | - | .5263 | 5.85 | 130 | $MnF_4$ 96.8 | Gray-blue solids |

TABLE 18. $LiMnF_5$ SYNTHESIS PRODUCT GAS COMPOSITION

| Compound | Mole Percent |
|---|---|
| $Cl_2$ | 60 |
| BrCl | 17 |
| HCl | 11 |
| $Br_2$ | 9 |
| HBr | 2 |

The color of the products obtained from the $LiF-MnCl_2-BrF_3$ reactions has not always been consistent, as noted in table 17. As a result, samples were submitted to determine d-spacings from their X-ray powder patterns. The d-spacings show similarities (as compiled in appendix C) but do not match exactly. The ASTM index does not contain a pattern or d-spacings for $LiMnF_5$. None of the patterns indicate the presence of LiF, $MnCl_2$, $MnF_2$, or $MnF_3$.

Three preparations were made using $MnBr_2$ as a reactant. As in the case of $MnCl_2$, it was found on the basis of weight change that the reaction product is $LiMnF_5$ with conversions of 94 to 99 percent. With $MnBr_2$, the heat of reaction was greater than with $MnCl_2$, but the gaseous product pressure buildup was less, due to the liberation of $Br_2$ instead of $Cl_2$ which has lower vapor pressure at ambient temperature.

Three reactions to prepare $MnF_4$ were made using only manganese halides and $BrF_3$ to obtain a better understanding of the $LiF-MnCl_2-BrF_3$ and $LiF-MnBr_2-BrF_3$ reactions. The divalent halides $MnF_2$, $MnCl_2$, and $MnBr_2$ were employed. The reaction product in each case was purplish-blue to gray-blue, consistent with the literature. The solid reaction products from the fluoride and bromide reactions corresponded to $MnF_4$ on a weight basis with conversions of 96 and 97 percent, respectively. However, the chloride reaction product calculated 112.3 percent conversion on the basis of $MnF_4$ and a more reasonable 101.7 percent if $MnF_5$ is assumed the product. In each case, the product appeared to be stable at ambient temperature.

The results of wet chemical analyses of the various reaction products, $LiMnF_5$ and $MnF_4$, have not been completely satisfactory. In no case has analysis accounted for 100 percent of the sample, the missing constituents amounting to from 10 to 25 percent of each of six samples. The possibility of incomplete conversion of $MnCl_2$ (or $MnBr_2$) was evaluated by analysis for chlorine and bromine but together these elements account for less than 1.5 percent of the sample. These data are thereby consistent with the X-ray diffraction data which showed no LiF, $MnCl_2$, or $MnBr_2$ in the samples. The analysis did provide expected lithium and manganese concentrations but effectively did not account for the active fluorine. A second approach to analysis by neutron activation analysis for Mn, F, and Br differed from the results obtained by wet chemical analysis by showing higher fluorine content.

The possibility of hydrolysis of the samples during handling is a plausible explanation for the analysis discrepancy. This possibility is consistent with the weight change during synthesis, the chemical reactivity of the resulting products, and the weight change on decomposition of $LiMnF_5$, as will be discussed later.

$LiMnF_5$ was found to be compatible with more fuels than the other reactants, as shown in table 19, but was not completely compatible with $Mg_3N_2$ nor $Ca_3N_2$. No significant endotherms were noted for $LiMnF_5$ mixtures up to the DTA limit of 500 C; however, decomposition could have occurred without an appreciable temperature change. Exotherms were noted with $NaN_3$, AlN, and $Ca_3N_2$. Upon mixing $LiMnF_5$ with either $Mg_3N_2$ or $Ca_3N_2$, some sparks were noted and in some cases the mixture would glow brightly for a few seconds.

A series of atmospheric pressure ignition and combustion tests was made with tamped mixtures of $LiMnF_5$ and selected fuels as shown in table 20. Complete combustion was obtained with a 90 weight percent $LiMnF_5$/10 weight percent $NaN_3$ mixture; however, a 95 weight percent $LiMnF_5$/4 weight percent $NaN_3$/1 weight percent Al composition would not sustain combustion. With magnesium as the fuel, sustaining combustion occurred with 5 weight percent Mg, but 2.5 weight percent Mg showed marginal combustion behavior.

TABLE 19. DTA OF $LiMnF_5$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $LiMnF_5$, (weight percent) | Endotherms, (C) | Exotherms, (C) |
|---|---|---|---|---|---|
| 1 | $NaN_3$ | 10.2 | 89.8 | - | 124s |
| 2 | AlN | 5.0 | 95.0 | - | 287vw |
| 3 | Al | 5.2 | 94.8 | - | - |
| 4 | $Ca_3N_2$ | 5.5 | 94.5 | - | 106wm |
| 5 | $Li_3N$ | 5.7 | 94.3 | - | - |
| 6 | Mg | 2.5 | 97.5 | - | - |
| 7 | Mg | 5.0 | 95.0 | - | - |
| 8 | $NaN_3$ | 9.8 | 90.2 | - | 123s |

NOTE: s = strong, wm = weak to medium, vw = very weak

Similarly, a 5 weight percent Al mixture burned well and a 2 weight percent Al composition did not. An AlN-$LiMnF_5$ mixture and an Fe-$LiMnF_5$ mixture both showed activity upon ignition but failed to sustain combustion.

Based on the ignition and combustion data, sensitivity tests were performed with a 90 weight percent $LiMnF_5$/10 weight percent $NaN_3$ composition and exhibited an impact sensitivity of 150 kg-cm and no friction sensitivity. A 95 weight percent $LiMnF_5$/5 weight percent Mg composition gave an impact sensitivity of 92.3 kg-cm and no friction sensitivity.

Difficulties encountered during preparation of $LiMnF_5$-$NaN_3$ grains were counter to the reasonable impact sensitivities noted above. Three of five $NaN_3$ grain preparations ignited during the pressing operation and burned to completion in the press. As noted in table 21, a 5 weight percent $NaN_3$ grain, successfully prepared, would not sustain combustion in the configuration tested. At 7.5 weight percent $NaN_3$, combustion could be obtained as noted in test No. 5. The exhaust from this test was passed through KI solution but since the KI-$F_2$ reaction is not quantitative, the

TABLE 20. IGNITION AND COMBUSTION TESTS OF $LiMnF_5$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $LiMnF_5$, (weight percent) | Results |
|---|---|---|---|---|
| 1 | $Mg_3N_2$ | 10.2 | 89.8 | Ignition occurred, combustion sustained |
| 2 | $Mg_3N_2$ | 10.3 | 89.7 | Sparks, red gas evolved on mixing |
| 3 | $NaN_3$ | 10.1 | 89.9 | Easy ignition, flame front moved evenly at moderate rate |
| 4 | $NaN_3$ | 4.0 | 95.0 | Not self-sustaining combustion |
| | Al | 1.0 | | |
| 5 | $Ca_3N_2$ | 5.3 | 94.7 | Red gas evolved on mixing; no visible combustion |
| 6 | Mg | 5.1 | 94.9 | Mixture ignited and burned rapidly, combustion complete |
| 7 | Mg | 2.5 | 97 5 | Partial combustion through center |
| 8 | Al | 5.1 | 94.9 | Easy ignition, combustion complete - fairly rapid burning rate |
| 9 | Al | 2.0 | 98.0 | Not self-sustaining combustion |
| 10 | AlN | 5.4 | 94.6 | Not self-sustaining combustion |
| 11 | Fe | 4.9 | 95.1 | Not self-sustaining combustion |

TABLE 21. GRAIN COMBUSTION TESTS OF $LiMnF_5$ AND VARIOUS FUELS

| Test No. | Fuel | Fuel Weight Percent | $LiMnF_5$, (weight percent) | Grain Weight, (g) | Grain Length, (in.) | Grain Density, (g/cc) | Burning Rate, (in./sec) | Glass Vessel, (1 atm) | Chamber Pressure, (psi) | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $NaN_3$ | 5.0 | 95.0 | 8.367 | .47 | 1.72 | - | - | X | Grain failed to burn, charred beneath igniter |
| 2 | $NaN_3$ | 10.0 | 90.0 | - | - | - | - | - | - | Spontaneous ignition during pressing |
| 3 | Mg | 2.5 | 97.5 | 11.864 | .54 | 2.11 | - | X | - | Grain burned only near nichrome igniter wire |
| 4 | Mg | 2.5 | 97.5 | 9.542 | .60 | 1.52 | - | X | - | Grain heated 150 C, very low burning rate; combustion complete |
| 5 | $NaN_3$ | 7.5 | 92.5 | 10.069 | .61 | 1.60 | - | X | - | Fired at ambient temperature, combustion essentially complete, fairly rapid burning rate |
| 6 | Mg | 2.5 | 97.5 | 12.684 | .70 | 1.73 | - | X | - | Grain heated 150 C, center of grain combusted |
| 7 | $NaN_3$ | 7.5 | 92.5 | - | - | - | - | - | - | Spontaneous ignition during pressing |
| 8 | $NaN_3$ | 7.5 | 92.5 | - | - | - | - | - | - | Spontaneious ignition during pressing |
| 9 | Mg | 2.5 | 97.5 | 14.458 | .82 | 1.69 | - | X | - | Ignited easily, but only approximately 1/4-in. of grain burned |

1.77 percent yield of fluorine from the grain based on evolved iodine is only an indication of fluorine generation.

Four grains were prepared from a 97.5 weight percent $LiMnF_5$/2.5 weight percent Mg composition. Two grains were tested at ambient temperature and pressure. The $LiMnF_5$ used for the first grain was prepared from the $LiF-MnCl_2-BrF_3$ reaction. The second grain, prepared with $LiMnF_5$ from the $LiF-MnBr_2-BrF_3$ reaction, appeared to ignite easier but in neither case was sustained combustion obtained. Two grains, prepared with $LiMnF_5$ from the $LiF-MnCl_2-BrF_3$ reaction, were fired at ambient pressure and at an elevated temperature of 150 C. The first grain ignited and burned completely but the burning rate was very low. The combustion gas products were swept into a KI solution with nitrogen. The liberated iodine calculated to be a 1.24 percent fluorine yield. The second grain ignited and combustion occurred in the center of the grain.

A sample of $LiMnF_5$ was exposed to air to determine the magnitude of the hydrolysis rate. A sample of $CoF_3$ of essentially the same weight was examined for comparison. Weight changes were taken as a measure of hydrolysis. Both samples appeared to reach a maximum weight increase after 20 to 24 hours, as shown in figure 5, and in the case of $LiMnF_5$, subsequent exposure caused a loss in weight. The conclusion which can be drawn is that $LiMn_5$ hydrolyzes slowly in air at a rate somewhat like that of $CoF_3$.

The thermal decomposition of $LiMnF_5$ was investigated under vacuum conditions. A sample was placed under a continuously maintained vacuum and the weight loss was measured at various temperatures. The data are listed in table 22. There was an initial weight loss at ambient temperature that could be interpreted as loss of residual $BrF_3$. The greatest weight loss occurred at 170 F and above; thus, $LiMnF_5$ appears to be fairly stable to thermal decomposition. After heating for a total of 20.7 hours at temperature levels of 125, 175, 225, and 300 F, 13.35 percent of the weight of the sample was lost. Correcting this value for the ambient temperature weight loss, the resulting figure of 12.24 percent corresponds closely to the value attributable to the loss of one fluorine (12.1 percent) from $LiMnF_5$.

TABLE 22. VACUUM[a] DECOMPOSITION OF LiF-$MnBr_2$-$BrF_3$ REACTION PRODUCT

Sample Weight = 4.568 g
Reactor Weight = 528.55 g

| Time, (min) | Temperature, (F) | Weight Loss, (g) | Cumulative Weight Loss, (g) | Percent Sample |
|---|---|---|---|---|
| 0 | 71 | - | - | - |
| 30 | 71 | .030 | .030 | .66 |
| 60 | 71 | .010 | .040 | .88 |
| 90 | 71 | .007 | .047 | 1.02 |
| 120 | 71 | .004 | .051 | 1.12 |
| 150 | 125 | .014 | .065 | 1.42 |
| 180 | 124 | .012 | .077 | 1.69 |
| 210 | 122 | .022 | .099 | 2.17 |
| 240 | 155 | .029 | .128 | 2.80 |
| 270 | 174 | .112 | .240 | 5.25 |
| 300 | 176 | .037 | .277 | 6.06 |
| 330 | 170 | .016 | .293 | 6.41 |
| 360 | 223 | .035 | .328 | 7.18 |
| 390 | 224 | .014 | .342 | 7.49 |
| 420 | 224 | .008 | .350 | 7.66 |
| 450 | 224 | .009 | .359 | 7.86 |
| 480 | 224 | .003 | .362 | 7.92 |
| 550 | 225 | .014 | .376 | 8.23 |
| 600 | 225 | .006 | .382 | 8.36 |
| 630 | 282 | .013 | .395 | 8.65 |
| 660 | 300 | .066 | .461 | 10.09 |
| 690 | 302 | .070 | .531 | 11.62 |
| 720 | 300 | .020 | .551 | 12.06 |
| 750 | 300 | .012 | .563 | 12.32 |
| 780 | 296 | .008 | .571 | 12.50 |
| 840 | 296 | .010 | .581 | 12.72 |
| 900 | 298 | .006 | .587 | 12.85 |
| 960 | 298 | .006 | .593 | 12.98 |
| 1020 | 302 | .002 | .595 | 13.03 |
| 1140 | 302 | .007 | .602 | 13.18 |
| 1200 | 297 | .005 | .607 | 13.29 |
| 1245 | 297 | .003 | .610 | 13.35 |

[a] Pressure of 200 microns.

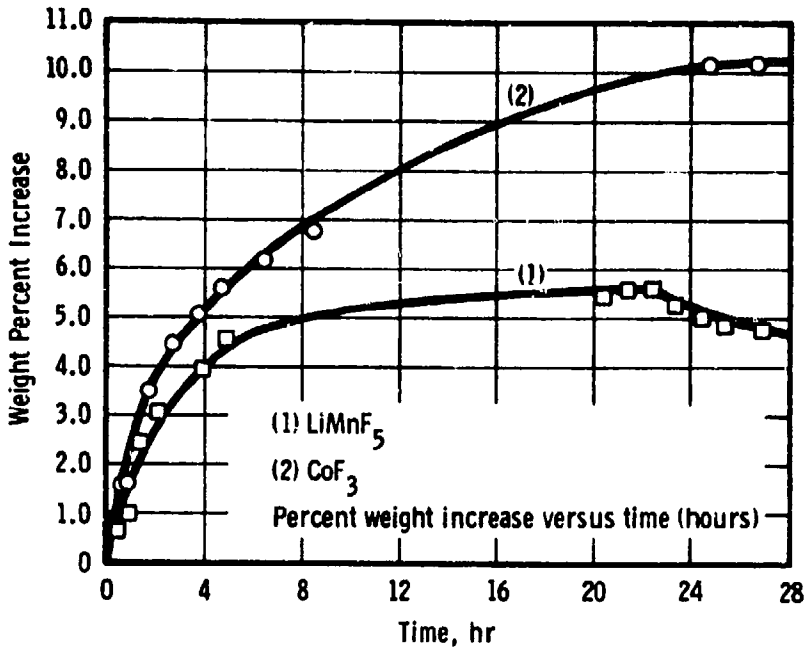


Figure 5. Air Hydrolysis Study

TASK 3: SCALABILITY TESTING AND SUPPORTING ANALYSIS

The objective of this task was to examine the scalability of the fluorine gas generation systems which were recommended as a consequence of the work of task 2. A specific objective of the program was development of a design of a generator producing .25 lb/sec of fluorine for a period of from 1 to 5 sec. An additional generator producing 5 lb/sec of fluorine for 10 sec was also designed.

During task 2 of the program, all candidates with the exception of $LiMnF_5$ had been eliminated from consideration on the basis ot production of interfering or deactivating species. $LiMnF_5$, on the other hand, produces essentially pure fluorine in the gas phase with the remainder forming a solid sintered residue. The fluorine yield of approximately 10 percent by weight is offset by the high purity of the fluorine available.

The results of task 2 showed that the fluorine-generating solid grains exhibited a uniformly low burning rate with only a modest pressure exponent. At approximately 100 psia, the burning rates of these gas generator grains were in the range of approximately .02 to .03 in./sec. At 1000 psia the

burning rate would typically be of the order of .05 in./sec. To utilize materials with such low burning rates at the flow rates and times specified in any reasonable geometry required a different design than normally considered in conventional gas generators. A solution to this type of system is the incorporation of discrete particles or pellets of the gas generator in a packed bed configuration with an igniter sized to ignite the entire bed. In this manner, high flow rates can be achieved through the large surface area available with the discrete particles. To achieve similar results with normal grain designs would require abnormally thin webs which are inconsistent with the physical properties of this type of gas generator.

The ignition of the pellet bed requires a more elaborate and effective technique than the experimental methods employed in the pressed grain experiments conducted earlier in the program. Although the hot wire type of igniter could eventually accomplish the ignition of all the gas generator material, extensive ignition delays and long rise times would be the consequence. A more appropriate ignition procedure involves a device producing a reactive gas with hot particles entrained to initiate combustion in a large fraction of the particles in the pellet bed. The hot particles serve to ignite a large number of pellets initially while the reactive gas serves to pressurize the system to promote combustion as well as to propagate the ignition by reaction with additional pellets.

In the case of the design point with the lower flow rates and shorter burning time, an igniter was employed which consisted of a fluorine gas generating formulation which burned at a higher temperature than the main gas generation grains. This material was a $KBrF_6$ formulation and was selected to produce a minimum of contamination during the ignition stage as well as its high temperature. The igniter stage was initiated by an electric squib initiator. In the case of the larger generator producing 5 lb of fluorine per second, an additional ignition stage was incorporated consisting of the standard fluorine gas generator formulation but with finer particle size to enhance mass flow rate. This stage was employed between the igniter grain and the gas generator grain. The design drawings for the generators are shown in figures 6 and 7, respectively.

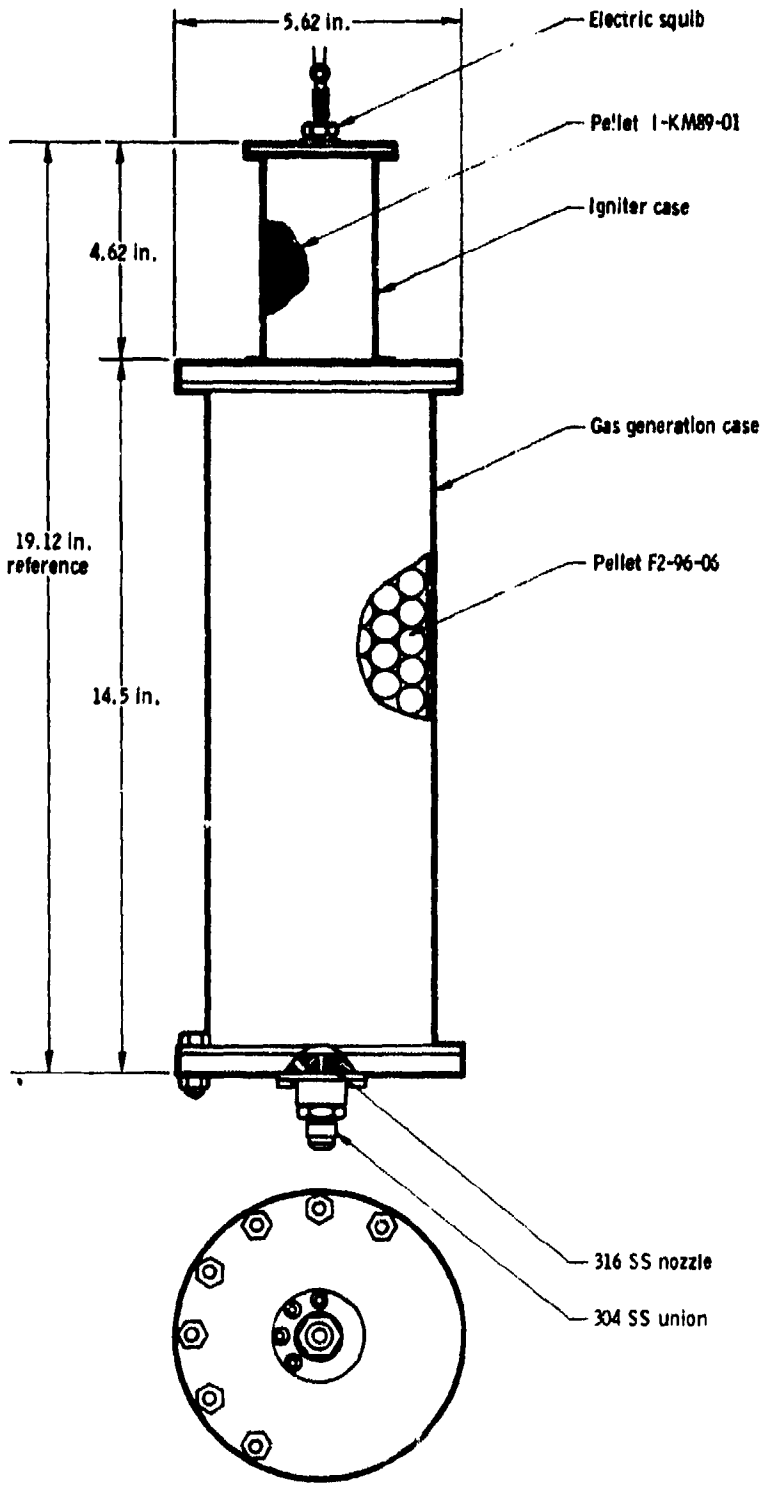


Figure 6. Smaller-Scale Fluorine Gas Generator Design

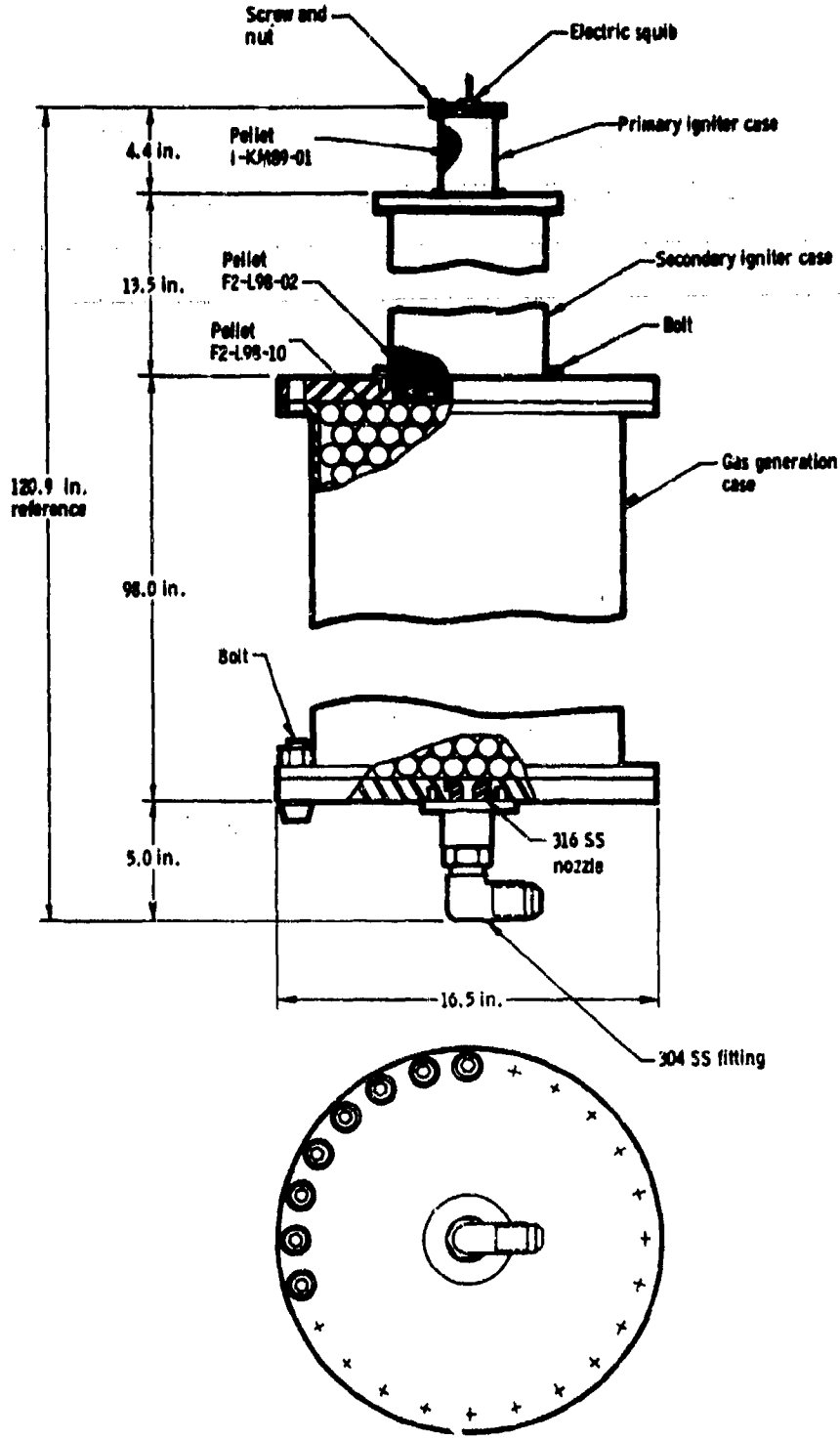


Figure 7. Larger-Scale Fluorine Gas Generator Design

Inconel-718 was selected for the material of construction since it embodied the best combination of properties required for the design requirements. It resists corrosion by fluorine and is frequently employed for this purpose. It further exhibits good strength-temperature relationships and should be adequate for the times involved in the requirements. Further, it is less expensive than other materials such as nickel which are sometimes employed to resist fluorine corrosion.

No filters are shown in the design sketches. These are conceived of as separate packages and, in view of the tendency of the gas generator grain to form a self-filtering clinker, may be of minimum size.

## CONCLUSIONS

The exploratory program described in this report was aimed at defining fluorine reactant systems from available or easily synthesized compounds that could be considered for chemical laser operations. The impact of the exhaust composition from candidate gas generators on overall laser system size and performance could not be quantitatively defined for many of the compositions considered in the program; therefore, subjective evaluations were made to reduce the number of candidates to a workable number consistent with the scope of the program.

The conclusions that can be drawn from the work reported earlier are as follows:

A. As a result of an in-depth literature review, a series of 32 candidate reactants were identified that potentialy met the minimum requirements for fluorine generation of 10 weight percent fluorine. Of these, 22 also potentially met the goal of 25 weight percent fluorine.

B. A list of 13 candidate reactants were identified that met realistic performance criteria primarily involving safety, stability, and cost. A large number of the original 32 candidates were rejected for safety considerations.

C. Of five reactants selected for experimental evaluation, small-scale grains were prepared and tested using $KBrF_6$, $KClF_4$, and $LiMnF_5$ as the fluorine-generating ingredient. Satisfactory combustion and ignition of $KBrF_6/Mg_3N_2$ and $KClF_4/AlN$ reactant systems was demonstrated.

D. A low-cost, one-step route for the preparation of $LiMnF_5$ was established. The compound was determined to be stable to decomposition under vacuum at temperatures up to approximately 160 F. Low hydrolysis rates observed in air were in agreement with the low apparent reactivity observed upon adding $LiMnF_6$ to water.

E. The compatibility of $LiMnF_5$ with various fuels was demonstrated. Ignition and combustion studies showed the feasibility of developing $LiMnF_5$ reactant systems that produce only fluorine as a

gaseous product. The fluorine yield for the candidate formulations is of the order of 10 weight percent.

F. The design of a fluorine gas generator using a $LiMnF_5/Mg$ composition showed the ignition system to be the area of greatest importance in scale-up.

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## APPENDIX A

## REACTANTS CONSIDERED LIST

The reactants considered list is composed of five tables depicting the properties of 32 candidate reactants. Table A-1 consists of a summary of the results of thermochemical equilibrium calculations conducted at temperatures of 300, 1000, 1500, and 2000 K and 1 atm pressure. These computer calculations effectively described the products of equilibrium dissociation of each reactant at each of the four designated temperatures. The data tabulated for each candidate include the weight percent fluorine available as F, $F_2$, and $NF_3$, and the $\alpha$ at 1500 K. Table A-2 contains the more important physical properties such as melting point, vapor pressure, decomposition temperature, preparation temperature, and heat of formation as well as chemical properties such as chemical reactivity and overall stability. These data were summarized from the literature. The decomposition temperature was generally that temperature where the material was reported to exhibit an appreciable dissociation pressure. The reported preparation temperatures were listed since, in some instances, these values depicted the overall thermal stability where more direct data were lacking. The heats of formation were estimated in many instances and are so noted.

Table A-3 lists availability data, the most common synthesis routes, and estimated costs for preparation of various quantities of each reactant from 10 to 10,000 lb. The availability assessment was made on a comparative basis of the commercial availability of precursors in the synthesis of each reactant and the complexity of synthesis. Costs were estimated based on labor and raw material costs only. As such, these costs presume existence of manufacturing facilities (e.g., no capitalization costs) and also do not include costs for process development. As a result, these costs are significantly less than can be expected, particularly for the very limited quantities included in this survey, and are presented for comparison purposes only.

Table A-4 is devoted to the properties which relate to potential hazards associated with the preparation and uses of the materials. These properties

include the reactivity with dry or moist air, the toxicity of precursors, and toxicity of the decomposition products. The data for this table were obtained from information developed from the literature search.

Table A-5 consists of a summary compilation of the thermochemical calculations of candidate reactant systems performed to evaluate the primary performance parameters of theoretical flame temperature, product composition, and weight percent fluorine.

TABLE A-1. FLUORINE YIELD OF REACTANTS
(RCL-1)

| Reactant No. | Reactant Composition | Fluorine Yield, (weight percent) 300 K | 1000 K | 1500 K | 2000 K | γ 1500 K | |
|---|---|---|---|---|---|---|---|
| 1 | $NF_4BF_4$ | 53.72 | 53.72 | 53.72 | 53.72 | 1.152 | |
| 2 | $XeF_6$ | 46.47 | 46.47 | 46.47 | 46.47 | 1.159 | |
| 3 | $2NOF \cdot XeF_6$ | 18.46 | 37.60 | 43.81 | 44.24 | 1.167 | |
| 4 | $KrF_2 \cdot XeF_6$ | 41.40 | 41.40 | 41.40 | 41.40 | 1.168 | |
| 5 | $NOClF_4$ | 6.25 | 32.34 | 39.97 | 45.13 | 1.177 | |
| 6 | $4XeF_6 \cdot MnF_4$ | 41.00 | 42.68 | 42.68 | 42.72 | 1.155 | |
| 7 | $4XeF_6 \cdot SnF_4$ | 38.78 | 38.78 | 38.78 | 38.78 | 1.157 | |
| 8 | $NOF \cdot XeOF_4$ | 19.65 | 34.40 | 40.10 | 40.51 | 1.177 | |
| 9 | $XeF_2 \cdot 2BrF_5$ | 7.32 | 15.75 | 36.03 | 38.26 | 1.140 | |
| 10 | $XeF_6 \cdot BF_3$ | 36.41 | 36.41 | 36.41 | 36.41 | 1.160 | |
| 11 | $NF_4AsF_6$ | 34.06 | 34.06 | 47.23 | 47.68 | 1.120 | |
| 12 | $(NO)_2MnF_6$ | 0 | 15.64 | 24.18 | 24.93 | 1.156 | |
| 13 | $KBrF_6$ | 16.30 | 30.94 | 32.06 | 34.66 | 1.095[a] | |
| 14 | $NF_3O \cdot SbF_5$ | 8.49 | 15.18 | 18.55 | 18.75 | 1.129 | |
| 15 | $NOBrF_4$ | 0 | 3.89 | 29.82 | 33.38 | 1.149 | |
| 16 | $XeF_2 \cdot XeF_4$ | 30.27 | 30.27 | 30.27 | 30.27 | – | |
| 17 | $BrF_6AsF_6$ | 9.93 | 15.52 | 38.98 | 40.65 | 1.118 | |
| 18 | $NOAsF_6$ | 0 | 4.85 | 25.42 | 26.02 | 1.124 | |
| 19 | $NF_4SbF_6$ | 29.16 | 29.16 | 29.16 | 29.16 | 1.131 | |
| 20 | $N_2F_3AsF_6$ | 27.74 | 27.74 | 41.23 | 41.62 | 1.125 | |
| 21 | $RbBrF_6$ | 0 | 8.19 | 26.81 | 28.91 | 1.148 | |
| 22 | $KClF_4$ | 0 | 24.89 | 25.29 | 30.42 | 1.095[a] | |
| 23 | $ClF_2BF_4$ | 0 | 23.49 | 23.77 | 28.52 | 1.166 | |
| 24 | $ClF_3O \cdot BF_3$ | 0 | 21.39 | 21.62 | 26.18 | 1.175 | |
| 25 | $CsBrF_6$ | 0 | 7.00 | 22.91 | 24.71 | 1.140 | |
| 26 | $XeF_2$ | 22.45 | 22.45 | 22.45 | 22.45 | 1.195 | |
| 27 | $NOVF_6$ | – | 5.80 | 18.17 | 19.48 | 1.103 | X |
| 28 | $XeF_2 \cdot MnF_4$ | – | 18.97 | 18.77 | 19.03 | 1.153 | X |
| 29 | $XeF_2 \cdot VF_5$ | – | 12.36 | 17.32 | 18.02 | 1.113 | X |
| 30 | $MnF_4$ | – | 14.50 | 14.23 | 14.63 | 1.077[a] | X |
| 31 | $LiMnF_5$ | – | 12.10 | 11.87 | 12.27 | 1.074[a] | X |
| 32 | $KMnF_5$ | – | 10.04 | 9.85 | 10.15 | 1.075[a] | X |

[a]Includes condensed phases.

TABLE A-2. STABILITY OF REACTANTS (RCL-2)

| Reactant No. | Reactant composition | Melting point, (C) | Prep. temperature, (C) | Decomposition temperature, (C) | $\Delta H_f^o$ (kcal/mole) | Vapor pressure | Chemical reactivity | Overall stability | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $NF_4BF_4$ | – | ~196 (by irradation) | >250 | -337.4 | nil at 25 C | Very reactive, strong oxidizer | Good in dry air, reacts with $H_2O$ | |
| 2 | $XeF_6$ | 49.5 | 120 | bp. 75.6 | -96.9 | 23.4mm Hg at 22.7 C | Stronger oxidizer than $XeF_2$ or $XeF_4$ | Reacts with glass, hazardous with $H_2O$ | (X) |
| 3 | $2NOF \cdot XeF_6$ | >130 | – | – | (-149) | ~10 mm Hg at 25 C | Extremely reactive | Hazardous with $H_2O$; fair stability | |
| 4 | $KrF_2 \cdot XeF_6$ | 40±2 | 20 | ~25 | (-101) | 11mm Hg at 20 C | Comparable to $XeF_6$ | Hazardous with $H_2O$; poor stability | |
| 5 | $NOClF_4$ | – | -23 | <0 | -69.2 | 1.4 atm at 0 C | Comparable to $ClF_3$ | Reacts with glass, $H_2O$; poor stability | X |
| 6 | $4XeF_6 \cdot MnF_4$ | – | 225 | >40 | (-650) | loses $XeF_6$ at 40 C in vac | (Comparable to $XeF_6$) | (Hazardous with $H_2O$; poor stability) | |
| 7 | $4XeF_6 \cdot SnF_4$ | – | 57 | 100 | (-679) | loses $XeF_6$ at 50 C in vac | Strong oxidizer, fluorinating agent | (Hazardous with $H_2O$; fair stability) | |
| 8 | $NOF \cdot XeOF_4$ | 40 | – | ~30 | (-42) | 30mm Hg at 23 C | (Very reactive) | (Hazardous; poor stability) | (X) |
| 9 | $XeF_2 \cdot 2BrF_5$ | ~23 | – | – | (-275) | – | (Very reactive) | Unknown, poor melting point | X |
| 10 | $XeF_6 \cdot BF_3$ | 90 | 25 | – | (-394) | <1mm Hg at 25 C | Comparable to $XeF_6$ | (Hazardous with $H_2O$; poor stability) | |
| 11 | $NF_4AsF_6$ | – | 200 | ~270 | (-335) | nil at 25 C | Very reactive, strong oxidizer | Good; corrosive, reacts with $H_2O$ | |
| 12 | $(NO)_2MnF_6$ | – | 100 | 150 | (-317) | nil at 25 C | (Comparable to NOF) | Good; corrosive, reacts with $H_2O$ | |
| 13 | $KBrF_6$ | – | 100 | ~250 | (-252) | nil at 25 C | Comparable with $BrF_5$ | Good; corrosive, reacts with $H_2O$ | |
| 14 | $NF_3O \cdot SbF_5$ | – | – | >25 | (-371) | – | Strong oxidizer | ($H_2O$ reactive) | |
| 15 | $NOBrF_4$ | 225 | 20 | >100 | (-98.6) | Some vp at 100 C | Strong oxidizer, very reactive | Good, corrosive, reacts with $H_2O$ | |
| 16 | $XeF_2 \cdot XeF_4$ | 90.2 | 340 to 380 | >25 | (-103) | Some vp at 25 C | Comparable to $XeF_4$ | (Hazardous with $H_2O$; fair stability) | |
| 17 | [illegible] | – | [illegible] to 25 | >20 | (-370) | Stable in vac | Very strong | (Good stability; | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10 | $XeF_6 \cdot BF_3$ | 90 | 25 | – | (-394) | <1mm Hg at 25 C | Comparable to $XeF_6$ | (Hazardous with $H_2O$; poor stability) | |
| | 11 | $NF_4AsF_6$ | – | 200 | ~270 | (-335) | nil at 25 C | Very reactive, strong oxidizer | Good; corrosive, reacts with $H_2O$ | |
| | 12 | $(NO)_2MnF_6$ | – | 100 | 150 | (-317) | nil at 25 C | (Comparable to NOF) | Good; corrosive, reacts with $H_2O$ | |
| | 13 | $KBrF_6$ | – | 100 | ~250 | (-252) | nil at 25 C | Comparable with $BrF_5$ | Good; corrosive, reacts with $H_2O$ | |
| | 14 | $NF_3O \cdot SbF_5$ | – | – | >25 | (-371) | – | Strong oxidizer | ($H_2O$ reactive) | |
| | 15 | $NOBrF_4$ | 225 | 20 | >100 | (-98.6) | Some vp at 100 C | Strong oxidizer, very reactive | Good, corrosive, reacts with $H_2O$ | |
| | 16 | $XeF_2 \cdot XeF_4$ | 90.2 | 340 to 380 | >25 | (-103) | Some vp at 25 C | Comparable to $XeF_4$ | (Hazardous with $H_2O$; fair stability) | |
| | 17 | $BrF_6AsF_6$ | – | low to 25 | >20 | (-370) | Stable in vac at 20 C | Very strong oxidizer | (Good stability; corrosive; reacts with $H_2O$) | |
| | 18 | $NOAsF_6$ | – | 94 | >100 | (-241) | Some vp at 200 C | Very reactive | Good; reacts with $H_2O$ | |
| σ | 19 | $NF_4SbF_6$ | – | 200 | 200 | (-403) | Slight at 200 C | Very strong oxidizer | Good; reacts with $H_2O$, corrosive | |
| | 20 | $N_2F_3AsF_6$ | – | -78 to 25 | >25 | (-269) | nil at 25 C | (Very strong oxidizer) | (Fair; corrosive, reacts with $H_2O$) | |
| | 21 | $RbBrF_6$ | – | 100 | ~300 | (-252) | nil at 25 C | Very strong oxidizer, comparable to $BrF_5$ | Good; reacts with $H_2O$, corrosive | |
| | 22 | $KClF_4$ | – | 100 | 200 | (-187) | nil at 25 C | Strong oxidizer, comparable to $ClF_3$ | Good, reacts with $H_2O$, corrosive | |
| | 23 | $ClF_2BF_4$ | 30 | -78 to 25 | ~10 | -334.1 | 550mm Hg at 5 C | Strong oxidizer, comparable to $ClF_3$ | Poor; high dissociation pressure | X |
| | 24 | $ClF_3O \cdot BF_3$ | – | -196 to 25 | >20 | (-326) | nil at 20 C | Comparable to $ClF_3$ | (Good; reactive) | |
| | 25 | $CsBrF_6$ | – | 100 | 300 | (-252) | nil at 25 C | Strong oxidizer, comparable to $BrF_5$ | Good; corrosive, high reactivity | |
| | 26 | $XeF_2$ | ~140 | 400 | ~25 | -40.5 | 4.55mm Hg at 25 C | Good oxidizer | Fair; high vapor pressure | (X) |
| | 27 | $NOVF_6$ | – | 20 | 60 | -396.2 | – | Strong oxidizer, similar to NOF | Good; reacts with $H_2O$ | |
| | 28 | $XeF_2 \cdot MnF_4$ | – | 120 | – | (-286) | – | (Comparable to $MnF_4$) | (Good; reacts with $H_2O$) | |
| | 29 | $XeF_2 \cdot VF_5$ | 38 | 90 | >90 | (-409) | <5mm Hg at 25 C | Potentially strong oxidizer | (Fair) | |
| | 30 | $MnF_4$ | – | 550 | ~25 | (-230) | – | Strong fluorinating agent | Fair; reacts with $H_2O$ | (X) |
| | 31 | $LiMnF_5$ | – | 350 | – | (-371) | nil at 25 C | (Comparable to $MnF_4$) | (Good, reacts with $H_2O$) | |
| | 32 | $KMnF_5$ | – | 20 | ~180 | (-381) | nil at 25 C | Comparable to $MnF_4$ | (Good; reactive) | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 15 | $NOBrF_4$ | 225 | 20 | >100 | (-98.6) | Some vp at 100 C | Strong oxidizer, very reactive | Good, corrosive, reacts with $H_2O$ | |
| 16 | $XeF_2 \cdot XeF_4$ | 90.2 | 340 to 380 | >25 | (-103) | Some vp at 25 C | Comparable to $XeF_4$ | (Hazardous with $H_2O$; fair stability) | |
| 17 | $BrF_6AsF_6$ | – | low to 25 | >20 | (-370) | Stable in vac at 20 C | Very strong oxidizer | (Good stability; corrosive; reacts with $H_2O$) | |
| 18 | $NOAsF_6$ | – | 94 | >100 | (-241) | Some vp at 200 C | Very reactive | Good; reacts with $H_2O$ | |
| 19 | $NF_4SbF_6$ | – | 200 | 200 | (-403) | Slight at 200 C | Very strong oxidizer | Good; reacts with $H_2O$, corrosive | |
| 20 | $N_2F_3AsF_6$ | – | -78 to 25 | >25 | (-269) | nil at 25 C | (Very strong oxidizer) | (Fair; corrosive, reacts with $H_2O$) | |
| 21 | $RbBrF_6$ | – | 100 | ~300 | (-252) | nil at 25 C | Very strong oxidizer, comparable to $BrF_5$ | Good; reacts with $H_2O$, corrosive | |
| 22 | $KClF_4$ | – | 100 | 200 | (-187) | nil at 25 C | Strong oxidizer, comparable to $ClF_3$ | Good, reacts with $H_2O$, corrosive | |
| 23 | $ClF_2BF_4$ | 30 | -78 to 25 | ~10 | -334.1 | 550mm Hg at 5 C | Strong oxidizer, comparable to $ClF_3$ | Poor; high dissociation pressure | X |
| 24 | $ClF_3O \cdot BF_3$ | – | -196 to 25 | >20 | (-326) | nil at 20 C | Comparable to $ClF_3$ | (Good; reactive) | |
| 25 | $CsBrF_6$ | – | 100 | 300 | (-252) | nil at 25 C | Strong oxidizer, comparable to $BrF_5$ | Good; corrosive, high reactivity | |
| 26 | $XeF_2$ | ~140 | 400 | ~25 | -40.5 | 4.55mm Hg at 25 C | Good oxidizer | Fair; high vapor pressure | (X) |
| 27 | $NOVF_6$ | – | 20 | 60 | -396.2 | – | Strong oxidizer, similar to NOF | Good; reacts with $H_2O$ | |
| 28 | $XeF_2 \cdot MnF_4$ | – | 120 | – | (-286) | – | (Comparable to $MnF_4$) | (Good; reacts with $H_2O$) | |
| 29 | $XeF_2 \cdot VF_5$ | 38 | 90 | >90 | (-409) | <5mm Hg at 25 C | Potentially strong oxidizer | (Fair) | |
| 30 | $MnF_4$ | – | 550 | ~25 | (-230) | – | Strong fluorinating agent | Fair; reacts with $H_2O$ | (X) |
| 31 | $LiMnF_5$ | – | 350 | – | (-371) | nil at 25 C | (Comparable to $MnF_4$) | (Good, reacts with $H_2O$) | |
| 32 | $KMnF_5$ | – | 20 | ~180 | (-381) | nil at 25 C | Comparable to $MnF_4$ | (Good; reactive) | |

Parentheses indicate estimated properties

TABLE A-3. REACTANT AVAILABILITY AND COST (RCL-3)

| Reactant No. | Reactant Composition | Availability | Synthesis Route | Cost, ($/lb) 10 lb | 100 lb | 1000 lb | 10,000 lb | Comments | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $NF_4BF_4$ | – | $NF_3 + F_2 + BF_3$ | >2000 | >1000 | – | – | Irradiation at -196 C | X |
| 2 | $XeF_6$ | C | $Xe + F_2$ | 1200 | 800 | 600 | 520 | 33 to 36 atm pressure | (X) |
| 3 | $2NOF \cdot XeF_6$ | D | $NOF + XeF_6$ | 920 | 700 | 490 | 410 | | (X) |
| 4 | $KrF_2 \cdot XeF_6$ | D | $KrF_2 + XeF_6$ | 1500 | 970 | 720 | 560 | $BrF_5$ solvent | (X) |
| 5 | $NOClF_4$ | A | $NOF + ClF_3$ | 190 | 118 | 61 | 31 | | |
| 6 | $4XeF_6 \cdot MnF_4$ | D | $Mn + F_2 + Xe$ | 1200 | 780 | 580 | 500 | | (X) |
| 7 | $4XeF_6 \cdot SnF_4$ | D | $SnF_4 + XeF_6$ | 1200 | 750 | 560 | 480 | | (X) |
| 8 | $NOF \cdot XeOF_4$ | D | $NOF + XeOF_4$ | 1250 | 820 | 650 | 550 | | (X) |
| 9 | $XeF_2 \cdot 2BrF_5$ | D | $XeF_2 + BrF_5$ | 625 | 490 | 320 | 275 | | (X) |
| 10 | $XeF_6 \cdot BF_3$ | C | $XeF_6 + BF_3$ | 950 | 725 | 540 | 450 | | (X) |
| 11 | $NF_4AsF_6$ | C | $NF_3 + F_2 + AsF_5$ | 495 | 355 | 215 | 140 | 35 atm pressure | |
| 12 | $(NO)_2MnF_6$ | B | $NOF + MnF_3 + BrF_3$ | 255 | 165 | 100 | 60 | | |
| 13 | $KBrF_6$ | B | $KF + BrF_5$ | 150 | 100 | 72 | 42 | | |
| 14 | $NF_3O \cdot SbF_5$ | D | $NF_3O + SbF_5$ | 190 | 120 | 75 | 50 | HF solvent | |
| 15 | $NOBrF_4$ | A | $NOF + BrF_3$ | 160 | 100 | 54 | 29 | | |
| 16 | $XeF_2 \cdot XeF_4$ | A | $Xe + F_2$ (99.9% Xe)<br>(92.94% Xe) | 1400<br>980 | 940<br>750 | 750<br>450 | 640<br>280 | 22 to 24 atm pressure | |
| 17 | $BrF_6AsF_6$ | C | $Kr_2F_3 \cdot AsF_6 + BrF_5$ | 290 | 210 | 130 | 90 | $BrF_5$ solvent | |
| 18 | $NOAsF_6$ | A | $NOF + AsF_5$ | 275 | 190 | 120 | 85 | | |
| 19 | $NF_4SbF_6$ | B | $NF_3 + F_2 + SbF_5$ | 270 | 175 | 105 | 78 | 85 atm pressure | |
| 20 | $N_2F_3AsF_6$ | B | $N_2F_4 + AsF_5$ | 770 | 480 | 260 | 165 | | (X) |
| 21 | $RbBrF_6$ | A | $RbF + BrF_5$ | 190 | 140 | 95 | 60 | | |
| 22 | $KClF_4$ | B | $KF + ClF_3$ | 105 | 70 | 51 | 30 | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 17 | $BrF_6AsF_6$ | C | $Kr_2F_3 \cdot AsF_6 + BrF_5$ | 290 | 210 | 130 | 90 | $BrF_5$ solvent | |
| 18 | $NOAsF_6$ | A | $NOF + AsF_5$ | 275 | 190 | 120 | 85 | | |
| 19 | $NF_4SbF_6$ | B | $NF_3 + F_2 + SbF_5$ | 270 | 175 | 105 | 78 | 85 atm pressure | |
| 20 | $N_2F_3AsF_6$ | B | $N_2F_4 + AsF_5$ | 770 | 480 | 260 | 165 | | (X) |
| 21 | $RbBrF_6$ | A | $RbF + BrF_5$ | 190 | 140 | 95 | 60 | | |
| 22 | $KClF_4$ | B | $KF + ClF_3$ | 105 | 70 | 51 | 30 | | |
| 23 | $ClF_2BF_4$ | A | $ClF_3 + BF_3$ | 65 | 39 | 26 | 20 | | |
| 24 | $ClF_3O \cdot BF_3$ | B | $ClF_3O + BF_3$ | 165 | 109 | 76 | 55 | | |
| 25 | $CsBrF_6$ | A | $CsF + BrF_5$ | 175 | 110 | 82 | 57 | | |
| 26 | $XeF_2$ | A | $Xe + F_2$ (99.9% Xe)<br>(92.94% Xe) | 1600<br>795 | 1100<br>610 | 920<br>390 | 700<br>295 | | (X) |
| 27 | $NOVF_6$ | A | $NOCl + V_2O_5$ | 510 | 310 | 160 | 82 | $BrF_3$ solvent | |
| 28 | $XeF_2 \cdot MnF_4$ | B[a] | $MnF_2 + XeF_2$ | 840 | 670 | 520 | 430 | | (X) |
| 29 | $XeF_2 \cdot VF_5$ | B | $XeF_2 + VF_5$ | 1220 | 750 | 530 | 440 | | (X) |
| 30 | $MnF_4$ | C | $MnF_3 + F_2$ | 76 | 48 | 34 | 27 | | |
| 31 | $LiMnF_5$ | D | $LiF + MnF_2 + F_2$ | 105 | 72 | 53 | 32 | | |
| 32 | $KMnF_5$ | B | $KMnO_4 + BrF_3$ | 90 | 61 | 45 | 24 | | |

[a]Yield not reported

Availability Legend:

A: Commercially available or easily synthesized (yield 75%)
B: Synthesis established (yield >50%)
C: Difficult synthesis (yield <50%)
D: Only milligram quantities prepared
F: Synthesis reported, yield and difficulty unknown

TABLE A-4. REACTANT

| Reactant No. | Reactant Composition | Reactivity with | | Precursor Toxicity | | |
|---|---|---|---|---|---|---|
| | | Dry Air | Moist Air | Compound | Threshold Limit Value | Comments |
| 1 | $NF_4BF_4$ | None | Forms HF, $NF_3$, and $BF_3$ | $NF_3$<br>$BF_3$<br>$F_2$ | 29<br>3 | Mildly toxic<br>Irritant<br>Reacts to form<br>for HF = 2 mg/m |
| 2 | $XeF_6$ | None | Forms hazardous products and HF | Xe<br>$F_2$ | N/A<br>.2 | Asphyxiant<br>Reacts to form |
| 3 | $2NOF \cdot XeF_6$ | (None) | (Forms hazardous products, HF and NOX) | $XeF_6$<br>NOF | —<br>— | See $XeF_6$<br>Reacts to form |
| 4 | $KrF_2 \cdot XeF_6$ | — | (Forms hazardous products and HF) | $KrF_2$<br>$XeF_6$ | —<br>— | Reacts to form<br>See $XeF_6$ |
| 5 | $NOClF_4$ | None | Forms HF, HCl, and NOX | NOF<br>$ClF_3$ | —<br>.4 | Reacts to form<br>Strong irritant; |
| 6 | $4XeF_6 \cdot MnF_4$ | (None) | (Forms hazardous products and HF) | $XeF_6$<br>$MnF_4$ | —<br>6 | See $XeF_6$<br>Dust, causes ne<br>system disorder |
| 7 | $4XeF_6 \cdot SnF_4$ | (None) | (Forms hazardous products and HF) | $XeF_6$<br>$SnF_4$ | —<br>(2) | See $XeF_6$<br>Toxic fumes on decomposition |
| 8 | $NOF \cdot XeOF_4$ | — | (Forms hazardous products and HF) | NOF<br>$XeOF_4$ | —<br>— | Reacts to form<br>(Strong irritant |
| 9 | $XeF_2 \cdot 2BrF_5$ | — | (Reacts to form HF) | $XeF_2$<br>$BrF_5$ | —<br>.4 | Toxic; irritant<br>Strong irritant |
| 10 | $XeF_6 \cdot BF_3$ | (None) | (Forms hazardous products and HF) | $XeF_6$<br>$BF_3$ | —<br>3 | See $XeF_6$<br>Irritant |
| 11 | $NF_4AsF_6$ | None | Reacts to form HF and toxic products | $NF_3$<br>$F_2$<br>$AsF_5$ | 29<br>.2<br><.1 | Mildly toxic<br>Reacts to form<br>Cumulative poi<br>(chronic syste |

4. REACTANT SAFETY (RCL-4)

| y | Decomposition Product Toxicity | | | |
|---|---|---|---|---|
| Comments | Compound | Threshold Limit Value | Comments | |
| ly toxic | $NF_3$ | 29 | Mildly toxic | |
| tant | $BF_3$ | 3 | Irritant | |
| ts to form HF, (TLV HF = 2 mg/m$^3$) | $F_2$ | .2 | Forms HF in moist air | |
| yxiant | Xe | N/A | Asphyxiant | |
| ts to form HF | $F_2$ | .2 | Forms HF in moist air | X |
| $XeF_6$ | Xe | N/A | Asphyxiant | |
| ts to form HF, NOX | $F_2$ | .2 | Forms HF in moist air | X |
| | $N_2$, $O_2$ | N/A | – | |
| ts to form HF | Kr | N/A | Asphyxiant | |
| $XeF_6$ | Xe | N/A | Asphyxiant | X |
| | $F_2$ | .2 | Forms HF in moist air | |
| ts to form HF | ClF | (.2) | Forms HCl and HF in moist air | |
| ng irritant; toxic | $F_2$ | .2 | Forms HF in moist air | |
| | $N_2$, $O_2$ | N/A | – | |
| $XeF_6$ | $F_2$ | .2 | Forms HF in moist air | |
| , causes nervous em disorders | Xe | N/A | Asphyxiant | X |
| | $MnF_3$ | 6 | Dust causes nervous system disorders | |
| | $MnF_2$ | 6 | | |
| $XeF_6$ | Xe | N/A | Asphyxiant | X |
| c fumes on mposition | $F_2$ | .2 | Forms HF in moist air | |
| | $SnF_2$ | (2) | Forms toxic fumes and HF in moist air | |
| | $SnF_4$ | (2) | | |
| ts to form HF ong irritant) | $F_2$ | .2 | Forms HF in moist air | X |
| | Xe | N/A | Asphyxiant | |
| | $O_2$, $N_2$ | N/A | – | |
| c; irritant | $F_2$ | .2 | Forms HF in moist air | |
| ng irritant, toxic | Xe | N/A | Asphyxiant | |
| | BrF | (.2) | Forms HF and HBr in moist air | |
| $XeF_6$ | Xe | N/A | Asphyxiant | X |
| tant | $F_2$ | .2 | Forms HF in moist air | |
| | $BF_3$ | 3 | Irritant | |
| ly toxic | $F_2$ | .2 | Forms HF in moist air | |
| ts to form HF | $N_2$ | N/A | – | |
| lative poison | $AsF_3$ | <.1 | Cumulative poison (chronic systemic) | X |
| onic systemic) | $AsF_5$ | <.1 | | |

TABLE A-4. (Contd.

| Reactant No. | Reactant Composition | Reactivity with Dry Air | Reactivity with Moist Air | Precursor Toxicity: Compound | Precursor Toxicity: Threshold Limit Value | Comments |
|---|---|---|---|---|---|---|
| 12 | $(NO)_2MnF_6$ | None | Forms HF and other irritants | NOF | – | Reacts to form HF |
| | | | | $MnF_4$ | 6 | Dust causes nervous system disorders |
| 13 | $KBrF_6$ | None | Forms HF and HBr | KF | 2.5 | Dust-irritant |
| | | | | $BrF_5$ | .4 | Strong irritant, toxic |
| 14 | $NF_3O \cdot SbF_5$ | (None) | Forms HF and poisonous Sb compounds | $NF_3O$ | – | Highly toxic $LD_{50}$ = 200 to 500 ppm |
| | | | | $SbF_5$ | .5 | Cumulative poison (chron systemic) |
| 15 | $NOBrF_4$ | None | Forms HF, HBr, NOX | NOF | – | Reacts to form HF |
| | | | | $BrF_3$ | .4 | Strong irritant, toxic |
| 16 | $XeF_2 \cdot XeF_4$ | (None) | (Forms hazardous compounds) | $XeF_2$ | – | Toxic, irritant |
| | | | | $XeF_4$ | – | Toxic, irritant |
| 17 | $BrF_6AsF_6$ | – | (Forms HF, HBr and As compounds) | $BrF_5$ | .4 | Strong irritant; toxic |
| | | | | $F_2$ | .2 | Reacts to form HF |
| | | | | $AsF_5$ | <.1 | Cumulative poison (chron systemic) |
| 18 | $NOAsF_6$ | (None) | (Forms HF, and hazardous As compounds) | NOF | – | Reacts to form HF |
| | | | | $AsF_5$ | .1 | Cumulative poison (chron systemic) |
| 19 | $NF_4SbF_6$ | None | Forms HF and poisonous Sb compounds | $NF_3$ | 29 | Mildly toxic |
| | | | | $F_2$ | .2 | Reacts to form HF |
| | | | | $SbF_5$ | .5 | Cumulative poison (chron systemic) |
| 20 | $N_2F_3AsF_6$ | – | (Forms HF and poisonous As compounds) | $N_2F_4$ | – | More toxic than $NF_3$; reacts to form HF with $H_2O$ |
| | | | | $AsF_5$ | <.1 | Cumulative poison (chron systemic) |
| | | | | $F_2$ | .2 | Reacts to form HF |
| 21 | $RbBrF_6$ | None | Forms HF and HBr | RbF | 2.5 | Irritant |
| | | | | $BrF_3$ | .4 | Strong irritant; toxic |

TABLE A-4. (Contd.)

| ity | Decomposition Product Toxicity | | | |
|---|---|---|---|---|
| Comments | Compound | Threshold Limit Value | Comments | |
| ects to form HF | $F_2$ | .2 | Forms HF in moist air | |
| ot causes nervous | $N_2$, $O_2$ | N/A | – | |
| stem disorders | $MnF_2$ | 6 | Dust causes nervous system disorders | |
| | $MnF_3$ | 6 | | |
| st-irritant | KF | 2.5 | Dust-irritant | |
| rong irritant, toxic | BrF | (.2) | Forms HF and HBr in moist air | |
| | $F_2$ | .2 | Forms HF in moist air | |
| ghly toxic | $NF_3$ | 29 | Mildly toxic | |
| 50 = 200 to 500 ppm | $O_2$ | N/A | – | (X) |
| mulative poison (chronic stemic) | $SbF_5$ | .5 | Cumulative poison (chronic systemic) | |
| ects to form HF | $N_2$, $O_2$ | N/A | – | |
| rong irritant, toxic | BrF | (.2) | Forms HF and HBr in moist air | |
| | $F_2$ | .2 | Forms HF in moist air | |
| tic, irritant | Xe | N/A | Asphyxiant | X |
| tic, irritant | $F_2$ | .2 | Forms HF in moist air | |
| rong irritant; toxic | $F_2$ | .2 | Forms HF in moist air | |
| | BrF | (.2) | Forms HBr and HF in moist air | X |
| ects to form HF | | | | |
| mulative poison (chronic stemic) | $AsF_3$ | <.1 | Cumulative poison (chronic systemic) | |
| ects to form HF | $F_2$ | .2 | Forms HF in moist air | X |
| mulative poison (chronic stemic) | $AsF_3$ | .1 | Cumulative poison (chronic systemic) | |
| dly toxic | $NF_3$ | 29 | Mildly toxic | |
| cts to form HF | $F_2$ | .2 | Forms HF in moist air | |
| mulative poison (chronic stemic) | $SbF_3$ | .5 | Cumulative poison (chronic systemic) | |
| | $SbF_5$ | .5 | | |
| e toxic than $NF_3$; | $NF_3$ | 29 | Mildly toxic | |
| cts to form HF with | $F_2$ | .2 | Forms HF in moist air | X |
| | $AsF_3$ | <.1 | Cumulative poison (chronic systemic) | |
| mulative poison (chronic stemic) | $AsF_5$ | <.1 | | |
| cts to form HF | | | | |
| itant | RbF | 2.5 | Irritant | |
| ong irritant; toxic | BrF | (.2) | Forms HF and HBr in moist air | |
| | $F_2$ | .2 | Forms HF in moist air | |

TABLE A-4.

| Reactant No. | Reactant Composition | Reactivity with Dry Air | Reactivity with Moist Air | Precursor Toxicity: Compound | Precursor Toxicity: Threshold Limit Value | Precursor Toxicity: Comments |
|---|---|---|---|---|---|---|
| 22 | $KClF_4$ | None | Forms HF and HCl | KF | 2.5 | Irritant |
| | | | | $ClF_3$ | .4 | Strong irritant; |
| 23 | $ClF_2BF_4$ | – | (Forms HF and HCl) | $ClF_3$ | .4 | Strong irritant; |
| | | | | $BF_3$ | 3 | Irritant |
| 24 | $ClF_3O \cdot BF_3$ | – | Forms HF and HCl | $BF_3$ | 3 | Irritant |
| | | | | $ClF_3O$ | – | (Probably similar $ClF_3$) |
| 25 | $CsBrF_6$ | None | Forms HF and HBr | CsF | 2.5 | Irritant |
| | | | | $BrF_5$ | .4 | Strong irritant; |
| 26 | $XeF_2$ | None | Forms HF | $XeF_2$ | – | Toxic; irritant |
| 27 | $NOVF_6$ | None | Forms HF, NOX and V compounds | NOF | – | Reacts to forms H |
| | | | | $VF_5$ | .5 | Strong irritant; |
| 28 | $XeF_2 \cdot MnF_4$ | (None) | (Forms HF) | $XeF_2$ | – | Toxic; irritant |
| | | | | $MnF_4$ | 6 | Dust causes nerve system disorders |
| 29 | $XeF_2 \cdot VF_5$ | – | (Forms HF and V compounds) | $XeF_2$ | – | Toxic; irritant |
| | | | | $VF_5$ | .5 | Strong irritant; |
| 30 | $MnF_4$ | None | Forms HF and Mn compounds | $MnF_4$ | 6 | Dust causes nerve system disorders |
| 31 | $LiMnF_5$ | (None) | Forms HF | LiF | 2.5 | Irritant |
| | | | | $MnF_4$ | 6 | Dust causes nerve system disorders |
| 32 | $KMnF_5$ | None | Forms HF | KF | 2.5 | Irritant |
| | | | | $MnF_4$ | 6 | Dust causes nerve system disorders |

a

NOTE: Estimated quantities are in parentheses.

TABLE A-4. (Contd.)

| or Toxicity | | Decomposition Product Toxicity | | |
|---|---|---|---|---|
| hold it ue | Comments | Compound | Threshold Limit Value | Comments |
| 5 | Irritant | KF | 2.5 | Irritant |
| | Strong irritant; toxic | ClF | (.2) | Irritant; forms HF and HCl |
| | | $F_2$ | .2 | Forms HF in moist air |
| | Strong irritant; toxic | $BF_3$ | 3 | Irritant |
| | | $F_2$ | .2 | Forms HF in moist air |
| | Irritant | ClF | .4 | Forms HF and HCl in moist air |
| | Irritant (Probably similar to $ClF_3$) | $BF_3$ | 3 | Irritant |
| | | ClF | (.2) | Forms HF and HCl in moist air |
| | | $F_2$ | .2 | Forms HF in moist air |
| | | $O_2$ | N/A | – |
| 5 | Irritant | CsF | 2.5 | Irritant |
| | Strong irritant; toxic | $F_2$ | .2 | Forms HF in moist air |
| | | BrF | (.2) | Forms HF and HBr in moist air |
| | | $BrF_3$ | (.2) | |
| | Toxic; irritant | Xe | N/A | Asphyxiant |
| | | $F_2$ | .2 | Forms HF in moist air |
| | Reacts to forms HF | $N_2$, $O_2$ | N/A | – |
| | | $F_2$ | .2 | Forms HF in moist air |
| | Strong irritant; toxic | $VF_3$ | .5 | Forms HF and V dust – respiratory irritant |
| | | $VF_5$ | .5 | |
| | Toxic; irritant | Xe | N/A | Asphyxiant |
| | Dust causes nervous system disorders | $F_2$ | .2 | Forms HF in moist air |
| | | $MnF_2$ | 6 | Dust causes nervous system disorders |
| | | $MnF_3$ | 6 | |
| | Toxic; irritant | Xe | N/A | Asphyxiant |
| | Strong irritant; toxic | $F_2$ | .2 | Forms HF in moist air |
| | | $VF_3$ | .5 | Forms HF and V compounds in moist air |
| | | $VF_5$ | .5 | |
| | Dust causes nervous system disorders | $F_2$ | .2 | Forms HF in moist air |
| | | $MnF_2$ | 6 | Dust causes nervous system disorders |
| | | $MnF_3$ | 6 | |
| 5 | Irritant | LiF | 2.5 | Irritant |
| | Dust causes nervous system disorders | $F_2$ | .2 | Forms HF in moist air |
| | | $MnF_2$ | 6 | Dust causes nervous system disorders |
| | | $MnF_3$ | 6 | |
| | Irritant | KF | 2.5 | Irritant |
| | Dust causes nervous system disorders | $F_2$ | .2 | Forms HF in moist air |
| | | $MnF_2$ | 6 | Dust causes nervous system disorders |
| | | $MnF_3$ | 6 | |

TABLE A-5. COMPARISON OF THEORETICAL CALCULATION RESULTS (RCL-5)

| Reactant | Fuel | Reactant Weight Percent | Flame Temperature, (K) | Weight Percent F, (F, $F_2$, $NF_3$) | Primary Gas Products |
|---|---|---|---|---|---|
| $(NO)_2MnF_6$ | $Si_3N_4$ | 93.0 | 1177 | 5.41 | $N_2$, NOF, $O_2$, $SiF_4$, $F_2$ |
| $KBrF_6$ | $Si_3N_4$ | 96.0 | 1015 | 2.36 | $BrF_3$, $BrF_5$, $SiF_4$, $N_2$, $F_2$ |
| $NF_3 \cdot SbF_5$ | $Si_3N_4$ | 95.0 | 1098 | 5.94 | $SbF_5$, NOF, $F_2$, $N_2$, $SiF_4$, $O_2$ |
| $NOBrF_4$ | $Si_3N_4$ | 95.0 | 1164 | 1.37 | $BrF_3$, $N_2$, $O_2$, NOF, $SiF_4$, $F_2$ |
| $NF_4SbF_6$ | $Si_3N_4$ | 95.0 | 1090 | 19.58 | $F_2$, $SbF_5$, $SiF_4$, $N_2$ |
| $RbBrF_6$ | $Si_3N_4$ | 96.0 | 1048 | 2.36 | $BrF_3$, $BrF_5$, $SiF_4$, $F_2$, $N_2$ |
| $KClF_4$ | $Si_3N_4$ | 95.0 | 973 | 11.61 | ClF, $F_2$, $SiF_4$, $ClF_3$, $N_2$ |
| $ClF_3O \cdot BF_3$ | $Si_3N_4$ | 95.0 | 1047 | 7.73 | $BF_3$, ClF, $O_2$, NOF, $SiF_4$ |
| $CsBrF_6$ | $Si_3N_4$ | 96.0 | 1112 | 2.84 | $BrF_3$, $SiF_4$, $F_2$, $N_2$, $BrF_5$ |
| $XeF_2$ | $Si_3N_4$ | 96.0 | 1018 | 15.05 | Xe, $F_2$, $SiF_4$, $N_2$ |
| $LiMnF_5$ | $Mg_3N_2$ | 99.0 | 921 | 10.86 | $F_2$, $N_2 = 10^{-5}$ |

## APPENDIX B

## THEORETICAL ANALYSIS OF REACTANT SYSTEM

The theoretical combustion parameters of candidate reactant systems were calculated using current JANNAF thermodynamic product data and heats of formation of reactants, where available. Chemical equilibrium was assumed throughout the calculations. An arbitrary chamber pressure of 100 psia was chosen for this analysis. The reactant systems included in the following tables are listed in the order of the experimental evaluation, as follows:

| System No. | Reactant | Fuel | Table |
|---|---|---|---|
| 2324 | $NOBrF_4$ | $Mg_3N_2$ | B-1 |
| 2314 | $NOBrF_4$ | $Si_3N_4$ | B-2 |
| 2018 | $NOBrF_4$ | $(C_2F_4)_n$ | B-3 |
| 2311 | $(NO)_2MnF_6$ | $Si_3N_4$ | B-4 |
| 2335 | $(NO)_2MnF_6$ | $(C_2F_4)_n$ | B-5 |
| 2325 | $(NO)_2MnF_6$ | $Mg_3N_2$ | B-6 |
| 2316 | $KBrF_6$ | $Si_3N_4$ | B-7 |
| 2334 | $KBrF_6$ | $(C_2F_4)_n$ | B-8 |
| 2326 | $KBrF_6$ | $Mg_3N_2$ | B-9 |
| 2343 | $KBrF_6/KF$ | $Mg_3N_2$ | B-10 |
| 2317 | $KClF_4$ | $Si_3N_4$ | B-11 |
| 2333 | $KClF_4$ | $(C_2F_4)_n$ | B-12 |
| 2349 | $KClF_4$ | $NaN_3$ | B-13 |
| 2327 | $KClF_4$ | $Mg_3N_2$ | B-14 |
| 2342 | $KClF_4/KF$ | $Mg_3N_2$ | B-15 |
| 2354 | $KClF_4$ | AlN | B-16 |
| 2359 | $KClF_4$ | Al | B-17 |
| 2321 | $LiMnF_5$ | $Si_3N_4$ | B-18 |
| 2336 | $LiMnF_5$ | $(C_2F_4)_n$ | B-19 |
| 2350 | $LiMnF_5$ | $NaN_3$ | B-20 |
| 2355 | $LiMnF_5$ | AlN | B-21 |
| 2301 | $LiMnF_5$ | Al | B-22 |
| 2385 | $LiMnF_5$ | Mg | B-23 |
| 2372 | $LiMnF_5$ | $Mg_3N_2$ | B-24 |
| 2344 | $KMnF_5$ | $Mg_3N_2$ | B-25 |

TABLE B-1. THEORETICAL ANALYSIS OF $NOBrF_4/Mg_3N_2$

| System No. 2324 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 |
|---|---|---|---|---|---|---|---|---|
| $NOBrF_4$, weight percent | 97.00 | 96.00 | 95.00 | 94.00 | 93.00 | 92.00 | 91.00 | 90 |
| $Mg_3N_2$, weight percent | 3.00 | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10 |
| Combustion parameters | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 10 |
| $T_c$ K | 751 | 1020 | 1181 | 1280 | 1352 | 1411 | 1469 | 15 |
| $\gamma$ | 1.123 | 1.103 | 1.088 | 1.084 | 1.084 | 1.087 | 1.092 | 1. |
| Moles gas/100 g | 1.072 | 1.087 | 1.153 | 1.241 | 1.338 | 1.439 | 1.541 | 1. |
| Combustion products, moles/100 g | | | | | | | | |
| F | – | .0049 | .0394 | .1005 | .1786 | .2691 | .3706 | .4 |
| $F_2$ | – | .0097 | .0422 | .0692 | .0891 | .1007 | .1022 | .0 |
| Br | – | – | – | – | – | – | .0002 | .0 |
| $Br_2$ | – | – | – | – | – | – | – | |
| BrF | .0010 | .0084 | .0434 | .1108 | .1895 | .2692 | .3450 | .4 |
| $BrF_3$ | .4283 | .4698 | .4568 | .3909 | .3091 | .2249 | .1440 | .0 |
| $BrF_5$ | .0924 | .0381 | .0108 | .0038 | .0016 | .0006 | .0002 | |
| $MgF_2$ | – | – | – | – | – | – | – | |
| $NF_3$ | – | .0007 | .0008 | .0006 | .0005 | .0003 | .0002 | .0 |
| NO | – | – | – | .0002 | .0003 | .0005 | .0007 | .0 |
| $N_2$ | .2104 | .2011 | .2281 | .2508 | .2683 | .2839 | .2990 | .3 |
| NOF | .1575 | .1921 | .1526 | .1218 | .1014 | .0847 | .0688 | .0 |
| $NO_2F$ | .0029 | .0005 | .0002 | .0001 | – | – | – | |
| $O_2$ | .1792 | .1615 | .1788 | .1915 | .1990 | .2045 | .2097 | .2 |
| $MgF_2(l)$ | – | – | – | – | – | – | – | .0 |
| $MgF_2(s)$ | .0892 | .1189 | .1486 | .1783 | .2080 | .2377 | .2674 | .2 |
| F, $F_2$, $NF_3$, weight percent | .00 | .50 | 2.40 | 4.58 | 6.81 | 8.96 | 10.93 | 12 |

THEORETICAL ANALYSIS OF $NOBrF_4/Mg_3N_2$

| | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|
| 00 | 93.00 | 92.00 | 91.00 | 90.00 | 89.00 | 88.00 | 87.00 | 86.00 | 85.00 |
| 00 | 7.00 | 8.00 | 9.00 | 10.00 | 11.00 | 12.00 | 13.00 | 14.00 | 15.00 |
| .0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 0 | 1352 | 1411 | 1469 | 1536 | 1571 | 1700 | 1913 | 2083 | 2199 |
| 84 | 1.084 | 1.087 | 1.092 | 1.000 | 1.107 | 1.136 | 1.134 | 1.110 | 1.101 |
| 41 | 1.338 | 1.439 | 1.541 | 1.638 | 1.644 | 1.699 | 1.700 | 1.696 | 1.705 |
| 05 | .1786 | .2691 | .3706 | .4810 | .5037 | .5961 | .6216 | .6134 | .6042 |
| 92 | .0891 | .1007 | .1022 | .0899 | .0734 | .0378 | .0110 | .0045 | .0026 | |
| - | - | - | .0002 | .0004 | .0007 | .0028 | .0198 | .0663 | .0137 |
| - | - | - | - | - | - | - | .0005 | .0022 | .0041 |
| 08 | .1895 | .2692 | .3450 | .4111 | .4333 | .4625 | .4465 | .3917 | .3252 |
| 09 | .3091 | .2249 | .1440 | .0725 | .0447 | .0079 | .0005 | .0001 | - |
| 38 | .0016 | .0006 | .0002 | - | - | - | - | - | - |
| - | - | - | - | - | - | .0003 | .0035 | .0159 | .0387 |
| 06 | .0005 | .0003 | .0002 | .0001 | - | - | - | - | - |
| 02 | .0003 | .0005 | .0007 | .0010 | .0012 | .0021 | .0044 | .0071 | .0094 |
| 08 | .2683 | .2839 | .2990 | .3147 | .3264 | .3437 | .3569 | .3647 | .3714 |
| 18 | .1014 | .0847 | .0688 | .0516 | .0425 | .0215 | .0071 | .0033 | .0021 |
| 01 | - | - | - | - | - | - | - | - | - |
| 15 | .1990 | .2045 | .2097 | .2154 | .2172 | .2246 | .2279 | .2257 | .2232 |
| - | - | - | - | .0033 | .3268 | .3563 | .3828 | .4001 | .4070 |
| 83 | .2080 | .2377 | .2674 | .2938 | - | - | - | - | - |
| 58 | .81 | 8.96 | 10.93 | 12.56 | 12.36 | 12.76 | 12.23 | 11.83 | 11.58 |

b

TABLE B-2. THEORETICAL ANALYSIS OF $NOBrF_4/Si_3N_4$

| System No. 2314 | 6 | 1 | 5 | 7 | 8 | 2 | 9 | 10 | 1 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|
| $NOBrF_4$, weight percent | 96.00 | 95.00 | 93.00 | 92.00 | 91.00 | 90.00 | 89.00 | 88.00 | 87.00 | 85.00 |
| $Si_3N_4$, weight percent | 4.00 | 5.00 | 7.00 | 8.00 | 9.00 | 10.00 | 11.00 | 12.00 | 13.00 | 15.00 |
| Combustion parameters | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 977 | 1165 | 1346 | 1411 | 1482 | 1588 | 1833 | 2067 | 2227 | 2569 |
| $\gamma$ | 1.129 | 1.097 | 1.089 | 1.093 | 1.103 | 1.133 | 1.173 | 1.132 | 1.127 | 1.155 |
| Moles gas/100 g | 1.179 | 1.249 | 1.465 | 1.583 | 1.700 | 1.803 | 1.840 | 1.848 | 1.872 | 1.907 |
| Combustion products, moles/100 g | | | | | | | | | | |
| F | .0017 | .0265 | .1519 | .2368 | .3331 | .4347 | .4811 | .4736 | .4771 | .4613 |
| $F_2$ | .0024 | .0223 | .0628 | .0711 | .0670 | .0435 | .0096 | .0027 | .0013 | .0004 |
| Br | - | - | - | .0001 | .0003 | .0011 | .0141 | .0818 | .1764 | .3617 |
| $Br_2$ | - | - | - | - | - | - | .0004 | .0034 | .0066 | .0063 |
| BrF | .0137 | .0655 | .2345 | .3216 | .4013 | .4610 | .4530 | .3847 | .2783 | .0829 |
| $BrF_3$ | .4812 | .4391 | .2648 | .1728 | .0878 | .0220 | .0007 | - | - | - |
| $BrF_5$ | .0215 | .0063 | .0009 | .0003 | .0001 | - | - | - | - | - |
| $NF_3$ | .0002 | .0004 | .0003 | .0002 | .0001 | - | - | - | - | - |
| NO | - | .0001 | .0004 | .0005 | .0008 | .0014 | .0037 | .0073 | .0107 | .0203 |
| $NO_2F$ | .0005 | .0002 | - | - | - | - | - | - | - | - |
| $N_2$ | .2394 | .2619 | .3045 | .3243 | .3449 | .3679 | .3903 | .4028 | .4132 | .4320 |
| NOF | .1509 | .1291 | .0901 | .0736 | .0554 | .0320 | .0081 | .0027 | .0014 | .0005 |
| $O_2$ | .1822 | .1906 | .2047 | .2101 | .2164 | .2251 | .2333 | .2314 | .2273 | .2156 |
| $SiF_4$ | .0855 | .1069 | .1497 | .1711 | .1925 | .2138 | .2352 | .2566 | .2780 | .3207 |
| F, $F_2$, $NF_3$, weight percent | .12 | 1.37 | 5.29 | 7.21 | 8.88 | 9.91 | 9.51 | 9.10 | 9.11 | 8.78 |

TABLE B-3. THEORETICAL ANALYSIS OF $NOBrF_4/(C_2F_4)_n$

| System No. 2081 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|---|
| $NOBrF_4$, weight percent | 60.00 | 65.00 | 70.00 | 75.00 | 80.00 | 85.00 | 87.50 | 90.00 |
| $(C_2F_4)_n$, weight percent | 40.00 | 35.00 | 30.00 | 25.00 | 20.00 | 15.00 | 12.50 | 10.00 |
| Combustion parameters | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 2199 | 2023 | 1907 | 1622 | 1352 | 1169 | 1012 | 798 |
| $\gamma$ | 1.103 | 1.086 | 1.086 | 1.138 | 1.093 | 1.102 | 1.125 | 1.135 |
| Moles gas/100 g | 1.463 | 1.472 | 1.467 | 1.499 | 1.392 | 1.241 | 1.194 | 1.168 |
| Combustion products, moles/100 g | | | | | | | | |
| F | .1851 | .1917 | .1623 | .1853 | .1031 | .0175 | .0016 | - |
| $F_2$ | .0003 | .0007 | .0009 | .0073 | .0283 | .0092 | .0011 | - |
| Br | .1584 | .0784 | .0450 | .0028 | - | - | - | - |
| $Br_2$ | .0079 | .0050 | .0035 | .0001 | - | - | - | - |
| BrF | .1486 | .2610 | .3244 | .3975 | .2881 | .1265 | .0575 | .0094 |
| $BrF_3$ | - | - | - | .0028 | .1419 | .3288 | .4090 | .4607 |
| $BrF_5$ | - | - | - | - | .0002 | .0019 | .0041 | .0140 |
| $CF_4$ | .5030 | .4870 | .5111 | .4994 | .3999 | .2999 | .2500 | .2000 |
| CO | .0018 | - | - | - | - | - | - | - |
| $COF_2$ | .2721 | .1976 | .0856 | .0005 | - | - | - | - |
| $CO_2$ | .0229 | .0151 | .0031 | - | - | - | - | - |
| $NF_3$ | - | - | - | - | - | .0001 | - | - |
| NO | .0004 | .0022 | .0025 | .0011 | .0003 | - | - | - |
| $N_2$ | .1611 | .1734 | .1864 | .1967 | .1918 | .1933 | .1985 | .2046 |
| NOF | - | .0005 | .0013 | .0088 | .0463 | .0703 | .0733 | .0739 |
| $O_2$ | .0012 | .0594 | .1404 | .1964 | .1917 | .1932 | .1984 | .2041 |
| F, $F_2$, $NF_3$, weight percent | 3.53 | 3.67 | 3.12 | 3.80 | 3.03 | .68 | .07 | .00 |

TABLE B-4. THEORETICAL ANALYSIS OF $(NO)_2MnF_6/Si_3N_4$

| System No. 2311 | 4 | 3 | 2 | 5 | 1 | 6 |
|---|---|---|---|---|---|---|
| $(NO)_2MnF_6$, weight percent | 80.00 | 85.00 | 90.00 | 93.00 | 95.00 | 96.00 |
| $Si_3N_4$, weight percent | 20.00 | 15.00 | 10.00 | 7.00 | 5.00 | 4.00 |
| Combustion parameters | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 2853 | 2207 | 1477 | 1177 | 891 | 692 |
| $\gamma$ | 1.093 | 1.113 | 1.094 | 1.086 | 1.080 | 1.084 |
| Moles gas/100 g | 1.564 | 1.654 | 1.435 | 1.233 | 1.056 | 1.001 |
| Combustion products, moles/100 g | | | | | | |
| F | .0135 | .0068 | .1975 | .0627 | .0021 | - |
| $F_2$ | - | - | .0291 | .1049 | .0303 | .0016 |
| $MnF_2$ | .1970 | .1747 | - | - | - | - |
| $MnF_3$ | .0109 | .1952 | .0608 | .0006 | - | - |
| $MnF_4$ | - | - | .0047 | .0014 | - | - |
| $NF_3$ | - | - | - | .0040 | .0330 | .0461 |
| $N_2$ | .6149 | .5775 | .5035 | .3371 | .1421 | .0663 |
| NOF | - | - | .0630 | .3331 | .6524 | .7634 |
| $O_2$ | .2438 | .3632 | .3607 | .2388 | .0858 | .0272 |
| NO | .0392 | .0153 | .0012 | .0001 | - | - |
| $SiF_3$ | .0229 | - | - | - | - | - |
| $SiF_4$ | .3895 | .3207 | .2138 | .1497 | .1069 | .0855 |
| $SiOF_2$ | .0159 | - | - | - | - | - |
| MnO (l) | .1404 | - | - | - | - | - |
| $MnF_2$(l) | - | .1440 | - | - | - | - |
| $MnF_3$(l) | - | - | .3276 | - | - | - |
| $MnF_3$(s) | - | - | - | .4042 | .4149 | .4193 |
| F, $F_2$, $NF_3$, weight percent | .26 | .12 | 4.86 | 5.41 | 3.18 | 2.69 |

TABLE B-5. THEORETICAL ANALYSIS OF $(NO)_2MnF_6/(C_2F_4)_n$

| System No. 2335 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $(NO)_2MnF_6$, weight percent | 60.00 | 65.00 | 70.00 | 75.00 | 80.00 | 85.00 | 90.00 |
| $(C_2F_4)_n$, weight percent | 40.00 | 35.00 | 30.00 | 25.00 | 20.00 | 15.00 | 10.00 |
| Combustion parameters | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1745 | 1626 | 1569 | 1483 | 1251 | 958 | 599 |
| $\gamma$ | 1.103 | 1.089 | 1.086 | 1.082 | 1.085 | 1.081 | 1.082 |
| Moles gas/100 g | 1.395 | 1.354 | 1.272 | 1.210 | 1.190 | 1.075 | .983 |
| Combustion products, moles/100 g | | | | | | | |
| F | .162 | .0077 | .0060 | .0072 | .0558 | .0042 | - |
| $F_2$ | - | - | - | - | .0318 | .0255 | .0001 |
| $CF_4$ | .4426 | .4558 | .4674 | .4869 | .3999 | .2999 | .2000 |
| $COF_2$ | .3001 | .2102 | .1203 | .1286 | - | - | - |
| $CO_2$ | .0572 | .0339 | .0122 | .0002 | - | - | - |
| $MnF_2$ | .0010 | .0004 | .0001 | - | - | - | - |
| $MnF_3$ | .2609 | .2167 | .1266 | .0548 | .0023 | - | - |
| $MnF_4$ | .0001 | .0001 | .0001 | .0002 | .0014 | - | - |
| NO | .0011 | .0012 | .0012 | .0010 | .0002 | - | - |
| ONF | .0002 | .0004 | .0007 | .0019 | .1264 | .4344 | .6883 |
| $N_2$ | .2614 | .2831 | .3048 | .3261 | .2859 | .1495 | .0247 |
| $NF_3$ | - | - | - | - | .0003 | .0075 | .0210 |
| $O_2$ | .0542 | .1441 | .2325 | .3195 | .2859 | .1524 | .0214 |
| $MnF_3(l)$ | - | .0667 | .1789 | .2726 | - | - | - |
| $MnF_3(s)$ | - | - | - | - | .3456 | .3712 | .3931 |
| F, $F_2$, $NF_3$, weight percent | .31 | .15 | .11 | .14 | 2.28 | 1.48 | 1.20 |

TABLE B-6. THEORETICAL ANALYSIS OF $(NO)_2MnF_6/Mg_3N_2$

| System No. 2325 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|
| $(NO)_2MnF_6$, weight percent | 97.00 | 96.00 | 95.00 | 94.00 | 93.00 | 92.00 | 91.00 | 90.00 |
| $Mg_3N_2$, weight percent | 3.00 | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10.00 |
| Combustion parameters | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 474 | 709 | 897 | 1039 | 1163 | 1276 | 1350 | 1424 |
| $\gamma$ | 1.079 | 1.075 | 1.072 | 1.075 | 1.079 | 1.081 | 1.000 | 1.087 |
| Moles gas/100 g | .895 | .918 | .960 | 1.032 | 1.111 | 1.189 | 1.234 | 1.278 |
| Combustion products, moles/100 g | | | | | | | | |
| F | - | - | .0028 | .0200 | .0657 | .1431 | .2034 | .2603 |
| $F_2$ | - | .0039 | .0504 | .1195 | .1575 | .1547 | .1275 | .0938 |
| $NF_3$ | .1048 | .0822 | .0579 | .0248 | .0086 | .0027 | .0011 | .0004 |
| $NOF_3$ | .0011 | .0003 | .0001 | - | - | - | - | - |
| $NO_2F$ | .0691 | .0965 | .0028 | .0013 | .0007 | .0003 | .0002 | .0001 |
| $N_2$ | .0130 | .0353 | .1005 | .1870 | .2740 | .3470 | .3912 | .4273 |
| ONF | .7058 | .7550 | .6671 | .5398 | .3936 | .2648 | .1891 | .1284 |
| $O_2$ | .0011 | .0320 | .0785 | .1392 | .2084 | .2687 | .3021 | .3280 |
| $MnF_3$ | - | - | - | - | .0004 | .0036 | .0125 | .0312 |
| $MnF_4$ | - | - | - | .0003 | .0014 | .0037 | .0060 | .0069 |
| $MgF_2(s)$ | .0891 | .1189 | .1486 | .1783 | .2080 | .2377 | .2675 | .2972 |
| $MnF_3(l)$ | - | - | - | - | - | - | .1815 | .3550 |
| $MnF_3(s)$ | .4237 | .4193 | .4149 | .4103 | .4044 | .3944 | .1970 | - |
| F, $F_2$, $NF_3$, weight percent | 5.97 | 4.84 | 5.27 | 6.34 | 7.72 | 8.75 | 8.77 | 8.53 |

TABLE 3-7. THEORETICAL ANALYSIS OF $KBrF_6/Si_3N_4$

| System No. 2316 | 6 | 1 | 5 | 8 | 7 | 2 | 9 | 10 | 11 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|
| $KBrF_6$, weight percent | 96.00 | 95.00 | 93.00 | 92.00 | 91.00 | 90.00 | 89.00 | 88.00 | 87.00 | 85.00 |
| $Si_3N_4$, weight percent | 4.00 | 5.00 | 7.00 | 8.00 | 9.00 | 10.00 | 11.00 | 12.00 | 13.00 | 15.00 |
| Combustion parameters | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1015 | 1126 | 1318 | 1395 | 1460 | 1530 | 1629 | 1753 | 1860 | 2252 |
| $\gamma$ | 1.058 | 1.067 | 1.073 | 1.077 | 1.082 | 1.090 | 1.102 | 1.110 | 1.136 | 1.126 |
| Moles gas/100 g | .613 | .724 | .883 | .997 | 1.117 | 1.235 | 1.341 | 1.436 | 1.541 | 1.598 |
| Combustion products, moles/100 g | | | | | | | | | | |
| F | .0077 | .0324 | .1294 | .2088 | .2963 | .3870 | .4578 | .4486 | .3840 | .3513 |
| $F_2$ | .0465 | .1030 | .1030 | .1036 | .0985 | .0810 | .0474 | .0178 | .0063 | .0008 |
| Br | - | - | - | - | .0001 | .0003 | .0010 | .0044 | .0146 | .1627 |
| $Br_2$ | - | - | - | - | - | - | - | .0001 | .0005 | .0058 |
| BrF | .0004 | .0031 | .0732 | .1571 | .2415 | .3156 | .3632 | .3708 | .3574 | .1893 |
| $BrF_3$ | .2323 | .3349 | .3217 | .2365 | .1486 | .0703 | .0177 | .2366 | .0003 | - |
| $BrF_5$ | .1793 | .0697 | .0042 | .0012 | .0004 | .0001 | - | - | - | - |
| KF | - | - | .0012 | .0035 | .0081 | .0181 | .0470 | .1290 | .2549 | .3414 |
| $K_2F_2$ | - | - | .0004 | .0013 | .0028 | .0060 | .0144 | .0358 | .0592 | .0114 |
| KBr | - | - | - | - | - | - | - | - | - | .0011 |
| $NF_3$ | .0078 | .0054 | .0007 | .0004 | .0002 | .0001 | - | - | - | - |
| $N_2$ | .0531 | .0686 | .0994 | .1139 | .1282 | .1425 | .1568 | .1711 | .1853 | .2138 |
| $SiF_4$ | .0855 | .1069 | .1497 | .1711 | .1925 | .2139 | .2352 | .2566 | .2780 | .3208 |
| KF(l) | - | - | - | .3888 | .3768 | .3561 | .3061 | .1772 | - | - |
| KF(s) | .4120 | .4076 | .3970 | - | - | - | - | - | - | - |
| F, $F_2$, $NF_3$, weight percent | 2.36 | 4.85 | 6.41 | 7.93 | 9.38 | 10.43 | 10.50 | 9.20 | 7.53 | 6.68 |

TABLE B-8. THEORETICAL ANALYSIS OF $KBrF_6/(C_2F_4)_n$

| System No. 2334 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| $KBrF_6$, weight percent | 65.00 | 70.00 | 75.00 | 80.00 | 85.00 | 90.00 |
| $(C_2F_4)_n$, weight percent | 35.00 | 30.00 | 25.00 | 20.00 | 15.00 | 10.00 |
| Combustion parameters | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 2025 | 1817 | 1521 | 1342 | 1131 | 919 |
| $\gamma$ | 1.110 | 1.097 | 1.087 | 1.072 | 1.000 | 1.059 |
| Moles gas/100 g | 1.186 | 1.145 | 1.053 | .882 | .725 | .594 |
| Combustion products, moles/100 g | | | | | | |
| F | .0049 | .0517 | .1884 | .0945 | .0209 | .0910 |
| $F_2$ | - | .0002 | .0244 | .0423 | .0393 | .0065 |
| Br | .1733 | .0379 | .0004 | - | - | - |
| BrF | .0179 | .2505 | .2960 | .1469 | .0903 | .0002 |
| $BrF_3$ | - | - | .0255 | .1956 | .3316 | .2064 |
| $BrF_5$ | - | - | .0001 | .0008 | .0242 | .1796 |
| $Br_2$ | .0302 | .0059 | - | - | - | - |
| $CF_4$ | .6996 | .5999 | .4999 | .3999 | .2999 | .2000 |
| KBr | .0270 | .0002 | - | - | - | - |
| KF | .2135 | .1575 | .0141 | .0016 | - | - |
| $K_2F_2$ | .0190 | .0414 | .0047 | .0006 | - | - |
| KF(l) | - | .0598 | .2983 | .3405 | .3363 | - |
| KF(s) | - | - | - | - | .0284 | .3863 |
| F, $F_2$, $NF_3$, weight percent | .09 | .99 | 4.51 | 3.40 | 1.89 | .27 |

TABLE B-9. THEORETICAL ANALYSIS OF $KBrF_6/Mg_3N_2$

| System No. 2326 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 |
|---|---|---|---|---|---|---|---|---|
| $KBrF_6$, weight percent | 97.00 | 96.00 | 95.00 | 94.00 | 93.00 | 92.00 | 91.00 | 90. |
| $Mg_3N_2$, weight percent | 3.00 | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10. |
| Combustion parameters | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 10 |
| $T_c$, K | 891 | 1029 | 1128 | 1195 | 1311 | 1392 | 1455 | 15 |
| $\gamma$ | 1.047 | 1.055 | 1.062 | 1.065 | 1.069 | 1.073 | 1.077 | 1. |
| Moles gas/100 g | .458 | .536 | .634 | .681 | .763 | .856 | .957 | 1. |
| Combustion products, moles/100 g | | | | | | | | |
| F | .0007 | .0100 | .0356 | .0635 | .1400 | .2290 | .3243 | .4 |
| $F_2$ | .0086 | .0687 | .1372 | .1521 | .1524 | .1486 | .1443 | .1 |
| BrF | -- | .0003 | .0020 | .0070 | .0419 | .1095 | .1847 | .2 |
| $BrF_3$ | .1055 | .2074 | .3109 | .3547 | .3487 | .2829 | .2050 | .1 |
| $BrF_5$ | .3108 | .2042 | .0948 | .0418 | .0086 | .0025 | .0009 | .0 |
| $N_2$ | .0272 | .0344 | .0458 | .0573 | .0687 | .0789 | .0890 | .0 |
| $NF_3$ | .0050 | .0103 | .0075 | .0043 | .0013 | .0006 | .0004 | .0 |
| KF | -- | -- | -- | .0001 | .0009 | .0029 | .0065 | .0 |
| $K_2F_2$ | -- | -- | -- | -- | .0004 | .0011 | .0023 | .0 |
| KF(l) | -- | -- | -- | .4032 | .3975 | .3898 | .3794 | .3 |
| KF(s) | .4163 | .4120 | .4076 | -- | -- | -- | -- | |
| $MgF_2$(l) | -- | -- | -- | -- | -- | -- | -- | |
| $MgF_2$(s) | .0891 | .1189 | .1486 | .1783 | .2080 | .2377 | .2675 | .2 |
| F, $F_2$, $NF_3$, weight percent | .62 | 3.39 | 6.32 | 7.23 | 8.55 | 10.03 | 11.66 | 13 |

ETICAL ANALYSIS OF $KBrF_6/Mg_3N_2$

| 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|
| 93.00 | 92.00 | 91.00 | 90.00 | 89.00 | 88.00 | 87.00 | 86.00 | 85.00 |
| 7.00 | 8.00 | 9.00 | 10.00 | 11.00 | 12.00 | 13.00 | 14.00 | 15.00 |
| 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 1311 | 1392 | 1455 | 1513 | 1537 | 1605 | 1693 | 1788 | 1881 |
| 1.069 | 1.073 | 1.077 | 1.081 | 1.083 | 1.089 | 1.097 | 1.102 | 1.115 |
| .763 | .856 | .957 | 1.061 | 1.075 | 1.162 | 1.240 | 1.314 | 1.389 |
| .1400 | .2290 | .3243 | .4254 | .4453 | .5331 | .5906 | .5892 | .5522 |
| .1524 | .1486 | .1443 | .1325 | .1163 | .0889 | .0533 | .0268 | .0127 |
| .0419 | .1095 | .1847 | .2565 | .2839 | .3337 | .3593 | .3618 | .3527 |
| .3487 | .2829 | .2050 | .1294 | .0977 | .0434 | .0125 | .0029 | .0007 |
| .0086 | .0025 | .0009 | .0003 | .0001 | – | – | – | – |
| .0687 | .0789 | .0890 | .0990 | .1089 | .1188 | .1288 | .1387 | .1486 |
| .0013 | .0006 | .0004 | .0002 | .0001 | – | – | – | – |
| .0009 | .0029 | .0065 | .0131 | .0168 | .0334 | .0724 | .1496 | .2526 |
| .0004 | .0011 | .0023 | .0044 | .0055 | .0104 | .0211 | .0403 | .0561 |
| .3975 | .3898 | .3794 | .3643 | .3541 | .3234 | .2589 | .1388 | – |
| – | – | – | – | – | – | – | – | – |
| – | – | – | – | .3269 | .3566 | .3861 | .4153 | .4437 |
| .2080 | .2377 | .2675 | .2972 | – | – | – | – | – |
| 8.53 | 10.03 | 11.66 | 13.13 | 12.89 | 13.51 | 13.25 | 12.21 | 10.98 |

b

## TABLE B-10. THEORETICAL ANALYSIS OF $KBrF_6$-(95/5)/$Mg_3N_2$

| System No. 2343 | 13 | 12 | 11 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $KBrF_6$-KF(95/5), weight percent | 87.0 | 88.0 | 89.0 | 90.0 | 91.0 | 92.0 | 93.0 | 94.0 | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| $Mg_3N_2$, weight percent | 13.0 | 12.0 | 11.0 | 10.0 | 9.0 | 8.0 | 7.0 | 6.0 | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| Combustion parameters | | | | | | | | | | | | | |
| Pc, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1726 | 1629 | 1553 | 1526 | 1465 | 1402 | 1321 | 1204 | 1131 | 1038 | 902 | 642 | 338 |
| γ | 1.097 | 1.090 | 1.083 | 1.081 | 1.076 | 1.072 | 1.068 | 1.064 | 1.000 | 1.054 | 1.045 | 1.045 | 1.047 |
| Moles gas/100 g | 1.192 | 1.120 | 1.037 | 1.025 | .923 | .822 | .730 | .650 | .603 | .517 | .439 | .419 | .414 |
| Combustion products, moles/100 g | | | | | | | | | | | | | |
| Br | .0021 | .0007 | .0003 | .0002 | - | - | - | - | - | - | - | - | - |
| BrF | .3454 | .3287 | .2853 | .2596 | .1902 | .1157 | .0468 | .0080 | .0021 | .0004 | - | - | - |
| $BrF_3$ | .0072 | .0294 | .0772 | .1070 | .1801 | .2574 | .3255 | .3410 | .3000 | .2080 | .1071 | .0595 | .0297 |
| $BrF_5$ | - | - | - | .0002 | .0007 | .0020 | .0068 | .0343 | .0855 | .1831 | .2883 | .3401 | .37 9 |
| F | .5556 | .5185 | .4381 | .4199 | .3203 | .2261 | .1393 | .0639 | .0343 | .0108 | .0009 | - | - |
| $F_2$ | .0392 | .0726 | .1024 | .1192 | .1526 | .1372 | .1398 | .1413 | .1278 | .0699 | .0099 | - | - |
| KF | .0886 | .0393 | .0187 | .0144 | .0071 | .0031 | .0010 | .0002 | - | - | - | - | - |
| $K_2F_2$ | .0251 | .0121 | .0061 | .0048 | .0025 | .0011 | .0004 | - | - | - | - | - | - |
| $NF_3$ | - | - | .0001 | .0002 | .0003 | .0005 | .0011 | .0036 | .0069 | .0097 | .0052 | - | - |
| $N_2$ | .1488 | .1188 | .1089 | .0950 | .0890 | .0790 | .0688 | .0576 | .0461 | .0348 | .0271 | .0198 | .0099 |
| KF (l) | .2908 | .3710 | .4085 | .4204 | .4374 | .4489 | .4574 | .4639 | .0909 | - | - | - | - |
| KF (s) | - | - | - | - | - | - | - | - | .3781 | .4740 | .4790 | .4839 | .4889 |
| $MgF_2$ (l) | .3860 | .3563 | .3269 | - | - | - | - | - | - | - | - | - | - |
| $MgF_2$ (s) | - | - | - | .2972 | .2675 | .2377 | .2080 | .1783 | .1486 | .1189 | .0892 | .0594 | .0297 |
| F, $F_2$, $NF_3$, weight percent | 12.04 | 12.60 | 12.22 | 12.52 | 11.14 | 9.54 | 8.02 | 6.79 | 5.90 | 3.41 | .69 | - | - |

TABLE B-11. THEORETICAL ANALYSIS OF $KClF_4/Si_3N_4$

| System No. 2317 | 6 | 1 | 7 | 5 | 8 | 9 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|
| $KClF_4$, weight percent | 96.00 | 95.00 | 94.00 | 93.00 | 92.00 | 91.00 | 90.00 | 85.00 |
| $Si_3N_4$, weight percent | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10.00 | 15.00 |
| Combustion parameters | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 838 | 973 | 1126 | 1205 | 1378 | 1554 | 1706 | 2174 |
| $\gamma$ | 1.081 | 1.087 | 1.096 | 1.094 | 1.098 | 1.102 | 1.100 | 1.119 |
| Moles gas/100 g | .975 | 1.115 | 1.217 | 1.236 | 1.297 | 1.351 | 1.411 | 1.780 |
| Combustion products, moles/100 g | | | | | | | | |
| F | .0022 | .0158 | .0716 | .1172 | .2547 | .3453 | .3326 | .2470 |
| $F_2$ | .1375 | .2502 | .2987 | .2480 | .1405 | .0483 | .0136 | .0005 |
| Cl | - | - | - | - | .0001 | .0011 | .0071 | .1998 |
| ClF | .4759 | .5909 | .6164 | .6145 | .6103 | .6014 | .5782 | .1802 |
| $ClF_3$ | .1618 | .0401 | .0080 | .0031 | .0005 | - | - | - |
| $Cl_2$ | - | - | - | - | .0001 | .0009 | .0062 | .0835 |
| KF | - | - | - | .0003 | .0037 | .0247 | .0907 | .4878 |
| $K_2F_2$ | - | - | - | .0001 | .0014 | .0081 | - | .0297 |
| $NF_3$ | .1108 | .0794 | .0168 | .0057 | .0005 | - | - | - |
| $N_2$ | .0016 | .0316 | .0771 | .0969 | .1138 | .1283 | .1426 | .2138 |
| $SiF_4$ | .0855 | .1069 | .1283 | .1497 | .1711 | .1925 | .2139 | .3208 |
| KCl | - | - | - | - | - | - | - | .0174 |
| KF(l) | - | - | - | .6172 | .6046 | .5636 | .4547 | - |
| KF(s) | .6377 | .6310 | .6242 | - | - | - | - | - |
| F, $F_2$, $NF_3$, weight percent | 11.58 | 11.61 | 13.67 | 11.98 | 10.21 | 8.40 | 6.84 | 4.71 |

TABLE B-12. THEORETICAL ANALYSIS OF $KClF_4/(C_2F_4)_n$

| System No. 2333 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| $KClF_4$, weight percent | 65.00 | 70.00 | 75.00 | 80.00 | 85.00 | 90.00 |
| $(C_2F_4)_n$, weight percent | 35.00 | 30.00 | 25.00 | 20.00 | 15.00 | 10.00 |
| Combustion parameters | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1985 | 1849 | 1711 | 1351 | 1040 | 772 |
| $\gamma$ | 1.103 | 1.097 | 1.087 | 1.090 | 1.096 | 1.073 |
| Moles gas/100 g | 1.312 | 1.125 | 1.146 | 1.134 | 1.129 | .898 |
| Combustion products, moles/100 g | | | | | | |
| F | .0065 | .0412 | .0872 | .1373 | .0297 | .0006 |
| $F_2$ | - | .0001 | .0011 | .0628 | .2348 | .1001 |
| $CF_4$ | .6979 | .5998 | .4999 | .4000 | .3000 | .2000 |
| Cl | .0958 | .0582 | .0162 | .0001 | - | - |
| ClF | .0124 | .1605 | .4055 | .5301 | .5496 | .3005 |
| $ClF_3$ | - | - | - | .0002 | .0150 | .2973 |
| $Cl_2$ | .1002 | .1197 | .0381 | .0002 | - | - |
| KCl | .1128 | .0067 | .0002 | - | - | - |
| KF | .2502 | .2105 | .0763 | .0023 | - | - |
| $K_2Cl_2$ | .0043 | - | - | - | - | - |
| $K_2F_2$ | .0301 | .0539 | .0219 | .0009 | - | - |
| KF(l) | - | .1398 | .3779 | .5273 | - | - |
| KF(s) | - | - | - | - | .5646 | .5978 |
| F, $F_2$, $NF_3$, weight percent | .12 | .79 | 1.70 | 4.99 | 9.49 | 3.82 |

TABLE B-13. THEORETICAL ANALYSIS OF $KClF_4/NaN_3$

| System No. 2349 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $KClF_4$, weight percent | 85.0 | 86.0 | 87.0 | 88.0 | 89.0 | 90.0 | 91.0 | 92.0 | 93.0 | 94.0 | 95.0 |
| $NaN_3$, weight percent | 15.0 | 14.0 | 13.0 | 12.0 | 11.0 | 10.0 | 9.0 | 8.0 | 7.0 | 6.0 | 5.0 |
| Combustion parameters | | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 997 | 959 | 920 | 877 | 828 | 768 | 695 | 613 | 530 | 450 | 371 |
| Moles gas/100 g | 1.220 | 1.170 | 1.119 | 1.069 | 1.023 | .983 | .948 | .916 | .880 | .837 | .790 |
| Combustion products, moles/100 g | | | | | | | | | | | |
| ClF | .5423 | .5406 | .5367 | .5296 | .5178 | .4986 | .4680 | .4215 | .3553 | .2701 | .1707 |
| $ClF_3$ | .0223 | .0306 | .0412 | .0549 | .0734 | .0992 | .1365 | .1896 | .2625 | .3542 | .4603 |
| F | .0200 | .0119 | .0065 | .0031 | .0011 | .0003 | — | — | — | — | — |
| $F_2$ | .2262 | .1817 | .1348 | .0893 | .0494 | .0202 | .0050 | .0006 | — | — | — |
| $NF_3$ | .1271 | .1635 | .1991 | .2310 | .2555 | .2676 | .2625 | .2395 | .2009 | .1493 | .0882 |
| $N_2$ | .2825 | .2412 | .2004 | .1613 | .1260 | .0969 | .0764 | .0648 | .0610 | .0638 | .0713 |
| KF(s) | .5645 | .5712 | .5779 | .5845 | .5912 | .5978 | .6045 | .6111 | .6177 | .6244 | .6310 |
| NaF(s) | .2307 | .2153 | .1999 | .1846 | .1692 | .1538 | .1384 | .1230 | .1077 | .0923 | .0769 |
| F, $F_2$, $NF_3$, weight percent | 16.22 | 16.45 | 16.59 | 16.62 | 16.46 | 16.02 | 15.15 | 13.68 | 11.45 | 8.51 | 5.02 |

TABLE B-14. THEORETICAL ANALYSIS OF $KClF_4/Mg_3N_2$

| System No. 2327 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|
| $KClF_4$, weight percent | 97.00 | 96.00 | 95.00 | 94.00 | 93.00 | 92.00 | 91.00 | 90.00 |
| $Mg_3N_2$, weight percent | 3.00 | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10.00 |
| Combustion parameters | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 715 | 832 | 958 | 1101 | 1169 | 1322 | 1464 | 1536 |
| $\gamma$ | 1.066 | 1.076 | 1.084 | 1.088 | 1.086 | 1.087 | 1.091 | 1.000 |
| Moles gas/100 g | .747 | .896 | 1.030 | 1.121 | 1.129 | 1.183 | 1.236 | 1.233 |
| Combustion products, moles/100 g | | | | | | | | |
| F | .0001 | .0022 | .0141 | .0619 | .1011 | .2391 | .3856 | .4201 |
| $F_2$ | .0432 | .1775 | .2956 | .3626 | .3352 | .2499 | .1438 | .0911 |
| ClF | .2217 | .4156 | .5703 | .6109 | .6133 | .6096 | .6035 | .5961 |
| $ClF_3$ | .4225 | .2220 | .0607 | .0134 | .0064 | .0013 | .0003 | .0001 |
| $ClF_5$ | .0001 | - | - | - | - | - | - | - |
| $NF_3$ | .0594 | .0788 | .0794 | .0260 | .0118 | .0017 | .0002 | .0001 |
| $N_2$ | - | .0002 | .0098 | .0464 | .0634 | .0784 | .0890 | .0990 |
| Cl | - | - | - | - | - | - | - | .0007 |
| $Cl_2$ | - | - | - | - | - | - | - | .0004 |
| KF | - | - | - | - | .0001 | .0017 | .0094 | .0191 |
| $K_2F_2$ | - | - | - | - | - | .0006 | .0033 | .0063 |
| KF(l) | - | - | - | - | .6174 | .6081 | .5884 | .5661 |
| KF(s) | .6443 | .6377 | .6310 | .6243 | - | - | - | - |
| $MgF_2$(l) | - | - | - | - | - | - | - | .2838 |
| $MgF_2$(s) | .0892 | .1189 | .1486 | .1783 | .2080 | .2377 | .2684 | .0134 |
| F, $F_2$, $NF_3$, weight percent | 5.03 | 11.27 | 16.03 | 16.44 | 15.33 | 14.14 | 12.81 | 11.44 |

TABLE B-15. THEORETICAL ANALYSIS OF $KClF_4$-KF(95/5)/$Mg_3N_2$

| System No. 2342 | 10 | 9 | 8 | 7 | 6 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| $KClF_4$-KF(95/5), weight percent | 90.0 | 91.0 | 92.0 | 93.0 | 94.0 | 95.0 | 96.0 | 97.0 | 98.0 |
| $Mg_3N_2$, weight percent | 10.0 | 9.0 | 8.0 | 7.0 | 6.0 | 5.0 | 4.0 | 3.0 | 2.0 |
| Combustion parameters | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1562 | 1492 | 1346 | 1191 | 1129 | 980 | 847 | 729 | 509 |
| $\gamma$ | 1.089 | 1.089 | 1.085 | 1.083 | 1.086 | 1.082 | 1.076 | 1.065 | 1.066 |
| Moles gas/100 g | 1.170 | 1.177 | 1.127 | 1.077 | 1.077 | .994 | .871 | .723 | .658 |
| Combustion products, moles/100 g | | | | | | | | | |
| Cl | .0009 | .0004 | - | - | - | - | - | - | - |
| ClF | .5658 | 5732 | 5794 | .5821 | .5837 | .5543 | .4215 | .2296 | .1189 |
| $ClF_3$ | - | .0002 | .0010 | .0048 | .0095 | .0452 | .1843 | .3824 | .4995 |
| $ClF_5$ | - | - | - | - | - | - | - | .0001 | - |
| $Cl_2$ | .0006 | .0003 | - | - | - | - | - | - | - |
| F | .4020 | .3821 | .2477 | .1104 | .0736 | .0173 | .0027 | .0002 | - |
| $F_2$ | .0706 | .1157 | .2162 | .3061 | .3413 | .2931 | .1836 | .0512 | - |
| KF | .0231 | .0117 | .0022 | .0002 | - | - | - | - | - |
| $K_2F_2$ | .0075 | .0041 | .0008 | - | - | - | - | - | - |
| NF3 | - | .0002 | .0012 | .0085 | .0182 | .0693 | .0785 | .0594 | .0396 |
| $N_2$ | .0990 | .0891 | .0786 | .0651 | .0503 | .0149 | .0004 | - | - |
| KF (l) | .6073 | .6326 | .6559 | .6665 | - | - | - | - | - |
| KF (s) | - | - | - | - | .6739 | .6812 | .6884 | .6956 | .7027 |
| $MgF_2$ (l) | .2971 | - | - | - | - | - | - | - | - |
| $MgF_2$ (s) | - | .2675 | .2377 | .2080 | .1783 | .1486 | .1189 | .0892 | .0594 |
| F, $F_2$, $NF_3$, weight percent | 10.32 | 11.67 | 12.99 | 14.21 | 15.40 | 15.42 | 11.50 | 5.33 | 2.26 |

TABLE B-16. THEORETICAL ANALYSIS OF $KClF_4$/AlN

| System No. 2354 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| $KClF_4$, weight percent | 90.0 | 91.0 | 92.0 | 93.0 | 94.0 | 95.0 | 96.0 | 97.0 | 98.0 |
| AlN, weight percent | 10.0 | 9.0 | 8.0 | 7.0 | 6.0 | 5.0 | 4.0 | 3.0 | 2.0 |
| Combustion parameters | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1785 | 1680 | 1510 | 1343 | 1163 | 1024 | 878 | 751 | 531 |
| $\gamma$ | 1.079 | 1.087 | 1.094 | 1.089 | 1.087 | 1.085 | 1.080 | 1.068 | 1.070 |
| Moles gas/100 g | 1.297 | 1.272 | 1.256 | 1.195 | 1.131 | 1.070 | .949 | .787 | .700 |
| Combustion products, moles/100 g | | | | | | | | | |
| $AlF_3$ | .0620 | .0237 | – | – | – | – | – | – | – |
| $Al_2F_6$ | .0004 | .0001 | – | – | – | – | – | – | – |
| Cl | .0106 | .0034 | .0005 | .0001 | – | – | – | – | – |
| ClF | .5733 | .5968 | .6098 | .6165 | .6177 | .6022 | .5007 | .2886 | .1464 |
| $ClF_3$ | – | – | .0002 | .0011 | .0067 | .0288 | .1370 | .3557 | .5045 |
| $ClF_5$ | – | – | – | – | – | – | – | .0001 | – |
| $Cl_2$ | .0069 | .0021 | .0003 | .0001 | – | – | – | – | – |
| F | .4553 | .4818 | .4176 | .2584 | .0964 | .0290 | .0045 | .0004 | – |
| $F_2$ | .0165 | .0380 | .1097 | .2294 | .3310 | .3213 | .2106 | .0689 | .0001 |
| KF | .0461 | .0155 | .0153 | .0022 | .0001 | – | – | – | – |
| $K_2F_2$ | .0040 | .0011 | .0051 | .0008 | .0001 | – | – | – | – |
| $NF_3$ | – | – | .0001 | .0013 | .0126 | .0556 | .0943 | .0731 | .0487 |
| $N_2$ | .1220 | .1098 | .0975 | .0847 | .0669 | .0332 | .0016 | – | – |
| KF(l) | – | – | – | .1015 | .1850 | – | – | – | – |
| KF(s) | – | – | – | – | – | .2651 | .3449 | .4247 | .5046 |
| $K_3AlF_6$(s) | .1813 | .1956 | .1952 | .1708 | .1464 | .1220 | .0976 | .0732 | .0488 |
| F, $F_2$, $NF_3$, weight percent | 9.28 | 10.60 | 12.11 | 13.70 | 15.13 | 15.93 | 13.46 | 6.79 | 2.78 |

TABLE B-17. THEORETICAL ANALYSIS OF $KClF_4$/Al

| System No. 2359 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $KClF_4$, weight percent | 90.0 | 91.0 | 92.0 | 93.0 | 94.0 | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| Al, weight percent | 10.0 | 9.0 | 8.0 | 7.0 | 6.0 | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| **Combustion parameters** | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 2153 | 2007 | 1977 | 1933 | 1861 | 1685 | 1394 | 1104 | 828 | 525 |
| $\gamma$ | 1.119 | 1.077 | 1.077 | 1.076 | 1.077 | 1.100 | 1.091 | 1.093 | 1.075 | 1.065 |
| Moles gas/100 g | 1.861 | 1.776 | 1.652 | 1.533 | 1.426 | 1.355 | 1.233 | 1.141 | .902 | .658 |
| **Combustion products, moles/100 g** | | | | | | | | | | |
| $AlClF_2$ | .0001 | – | – | – | – | – | – | – | – | – |
| $AlF_3$ | .3685 | .3182 | .2322 | .1476 | .0659 | .0008 | – | – | – | – |
| $Al_2F_6$ | .0010 | .0017 | .0012 | .0007 | .0002 | – | – | – | – | – |
| Cl | .1715 | .0856 | .0618 | .0391 | .0190 | .0032 | .0001 | – | – | – |
| ClF | .2815 | .4160 | .4775 | .5349 | .5853 | .6245 | .6366 | .6289 | .3608 | .0561 |
| $ClF_3$ | – | – | – | – | – | – | .0008 | .0154 | .2901 | .6014 |
| $Cl_2$ | .0677 | .0498 | .0352 | .0216 | .0100 | .0017 | .0001 | – | – | – |
| F | .4067 | .3945 | .4588 | .5248 | .5892 | .6041 | .3508 | .0698 | .0024 | – |
| $F_2$ | .0013 | .0026 | .0044 | .0078 | .0158 | .0542 | .2392 | .4272 | .2484 | .0003 |
| KCl | .0093 | .0031 | .0014 | .0005 | .0001 | – | – | – | – | – |
| KF | .5173 | .4434 | .3345 | .2271 | .1254 | .0543 | .0043 | – | – | – |
| $K_2F_2$ | .0356 | .0611 | .0448 | .0292 | .0154 | .0117 | .0016 | – | – | – |
| KF(l) | – | – | – | – | – | – | .1855 | – | – | – |
| KF(s) | – | – | – | – | – | – | – | .3106 | .4286 | .5464 |
| $K_3AlF_6$(s) | – | .0119 | .0619 | .1106 | .1560 | .1845 | .1483 | .1112 | .0741 | .0371 |
| F, $F_2$, $KF_3$, weight percent | 7.78 | 7.59 | 8.88 | 10.27 | 11.79 | 13.54 | 15.75 | 17.56 | 9.48 | .01 |

TABLE B-18. THEORETICAL ANALYSIS OF $LiMnF_5/Si_3N_4$

| System No. 2321 | 1 | 2 | 3 |
|---|---|---|---|
| $LiMnF_5$, weight percent | 95.00 | 90.00 | 85.00 |
| $Si_3N_4$, weight percent | 5.00 | 10.00 | 15.00 |
| Combustion parameters | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1395 | 1806 | 2067 |
| Moles gas/100 g | .314 | .682 | .777 |
| Combustion products, moles/100 g | | | |
| F | .0796 | .0036 | – |
| $F_2$ | .0476 | – | – |
| LiF | .0001 | .0184 | .1257 |
| $Li_2F_2$ | .0001 | .0089 | .0442 |
| $Li_3F_3$ | – | .0014 | .0070 |
| Mn | – | – | .0284 |
| $MnF_2$ | – | .0051 | .0372 |
| $MnF_3$ | .0056 | .2884 | – |
| $MnF_4$ | .0022 | – | – |
| $NF_3$ | .0003 | – | – |
| $N_2$ | .0711 | .1426 | .2139 |
| $SiF_3$ | – | – | .0286 |
| $SiF_4$ | .1069 | .2139 | .2921 |
| LiF (1) | .6052 | .5331 | .3066 |
| Mn (1) | – | – | .0569 |
| $MnF_2$ (1) | – | – | .4193 |
| $MnF_3$ (1) | .5978 | .2803 | – |
| F, $F_2$, $NF_3$, weight percent | 3.34 | .07 | – |

TABLE B-19. THEORETICAL ANALYSIS OF $LiMnF_5/(C_2F_4)_n$

| System No. 2336 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|
| $LiMnF_5$, weight percent | 90.00 | 95.00 | 96.00 | 97.00 | 98.00 | 99.00 | 99.10 | 99.20 | 99.30 | 99.40 |
| $(C_2F_4)_n$, weight percent | 10.00 | 5.00 | 4.00 | 3.00 | 2.00 | 1.00 | .90 | .80 | .70 | .60 |
| Combustion parameters | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1307 | 1070 | 996 | 918 | 837 | 752 | 744 | 735 | 726 | 718 |
| $\gamma$ | 1.027 | 1.024 | 1.023 | 1.022 | 1.022 | 1.023 | 1.023 | 1.023 | 1.023 | 1.023 |
| Moles gas/100 g | .317 | .312 | .311 | .311 | .313 | .316 | .316 | .316 | .316 | .317 |
| Combustion products, moles/100 g | | | | | | | | | | |
| F | .0549 | .0184 | .0099 | .0046 | .0017 | .0005 | .0004 | .0004 | .0003 | .0003 |
| $F_2$ | .0587 | .1934 | .2210 | .2469 | .2715 | .2953 | .2976 | .3000 | .3023 | .3047 |
| $CF_4$ | .2000 | .1000 | .0800 | .0600 | .0400 | .0200 | .0180 | .0160 | .0140 | .0120 |
| $MnF_3$ | .0016 | - | - | - | - | - | - | - | - | - |
| $MnF_4$ | .0016 | .0003 | .0001 | - | - | - | - | - | - | - |
| LiF(l) | .5736 | - | - | - | - | - | - | - | - | - |
| LiF(s) | - | .6056 | .6120 | .6183 | .6247 | .6311 | .6317 | .6324 | .6330 | .6336 |
| $MnF_3$(s) | .5706 | .6053 | .6118 | .6183 | .6247 | .6311 | .6317 | .6324 | .6330 | .6336 |
| F, $F_2$, $NF_3$, weight percent | 3.27 | 7.70 | 8.58 | 9.47 | 10.35 | 11.23 | 11.32 | 11.41 | 11.49 | 11.63 |

TABLE B-20. THEORETICAL ANALYSIS OF $LiMnF_5/NaN_3$

| System No. 2350 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $LiMnF_5$, weight percent | 90.0 | 91.0 | 92.0 | 93.0 | 94.0 | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| $NaN_3$, weight percent | 10.0 | 9.0 | 8.0 | 7.0 | 6.0 | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| Combustion parameters | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1207 | 1161 | 1121 | 1121 | 1111 | 1070 | 1028 | 982 | 909 | 791 |
| $\gamma$ | 1.040 | 1.040 | 1.000 | 1.000 | 1.040 | 1.040 | 1.038 | 1.034 | 1.020 | 1.020 |
| Moles gas/100 g | .459 | .429 | .398 | .385 | .367 | .331 | .295 | .262 | .254 | .285 |
| Combustion products, moles/100 g | | | | | | | | | | |
| F | .0585 | .0417 | .0294 | .0297 | .0273 | .0177 | .0109 | .0063 | .0030 | .0008 |
| $F_2$ | .1619 | .1678 | .1664 | .1753 | .1809 | .1690 | .1523 | .1379 | .1596 | .2383 |
| $MnF_3$ | .0004 | .0001 | .0001 | .0001 | - | - | - | - | - | - |
| $MnF_4$ | .0014 | .0009 | .0006 | .0006 | .0005 | .0003 | .0002 | .0001 | - | - |
| $NF_3$ | .0121 | .0211 | .0335 | .0348 | .0391 | .0575 | .0783 | .0967 | .0906 | .0461 |
| $N_2$ | .2247 | .1971 | .1678 | .1441 | .1188 | .0866 | .0532 | .0208 | .0009 | - |
| LiF(l) | .5737 | .5801 | .5603 | .2448 | - | - | - | - | - | - |
| LiF(s) | - | - | .0261 | .3481 | .5992 | .6056 | .6120 | .6183 | .6247 | .6311 |
| $MnF_3$(s) | .5719 | .5790 | .5858 | .5922 | .5987 | .6053 | .6118 | .6183 | .6247 | .6311 |
| NaF(s) | .1538 | .1384 | .1230 | .1077 | .0923 | .0769 | .0615 | .0461 | .0308 | .0154 |
| F, $F_2$, $NF_3$, weight percent | 7.95 | 8.37 | 8.79 | 9.21 | 9.62 | 10.04 | 10.45 | 10.87 | 11.2° | 11.70 |

TABLE B-21. THEORETICAL ANALYSIS OF $LiMnF_5$/AlN

| System No. 2355 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $LiMnF_5$, weight percent | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| AlN, weight percent | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| **Combustion parameters** | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1364 | 1350 | 1195 | 1105 | 930 |
| $\gamma$ | 1.025 | 1.000 | 1.027 | 1.028 | 1.019 |
| Moles gas/100 g | .221 | .254 | .247 | .252 | .269 |
| **Combustion products, moles/100 g** | | | | | |
| F | .0736 | .0868 | .0398 | .0223 | .0048 |
| $F_2$ | .0803 | .1126 | .1643 | .1939 | .2401 |
| $LiAlF_4$ | - | .0002 | - | - | - |
| $MnF_3$ | .0027 | .0026 | .0002 | - | - |
| $MnF_4$ | .0022 | .0026 | .0009 | .0004 | - |
| $NF_3$ | .0011 | .0015 | .0098 | .0226 | .0243 |
| $N_2$ | .0605 | .0480 | .0317 | .0131 | - |
| LiF(l) | .2398 | .3194 | .3988 | - | - |
| LiF(s) | - | - | - | .4783 | .5579 |
| $Li_3AlF_6$(l) | .1218 | .0974 | .0732 | .0488 | - |
| $Li_3AlF_6$(s) | - | - | - | - | .0234 |
| $MnF_3$(l) | .6007 | .0079 | - | - | - |
| $MnF_3$(s) | - | .5988 | .6172 | .6243 | .6310 |
| F, $F_2$, $NF_3$, weight percent | 4.51 | 6.01 | 7.56 | 9.08 | 10.60 |

TABLE B-22. THEORETICAL ANALYSIS OF $LiMnF_5$/Al

| System No. 2361 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $LiMnF_5$, weight percent | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| Al, weight percent | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| Combustion parameters | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1857 | 1735 | 1480 | 1328 | 1079 |
| $\gamma$ | 1.098 | 1.063 | 1.032 | 1.028 | 1.021 |
| Moles gas/100 g | .424 | .264 | .218 | .249 | .271 |
| Combustion products, moles/100g | | | | | |
| $AlF_3$ | .0036 | .0008 | - | - | - |
| F | .0488 | .1431 | .1275 | .0891 | .0210 |
| $F_2$ | .0004 | .0110 | .0771 | .1554 | .2493 |
| $LiAlF_4$ | .0211 | .0065 | .0007 | .0001 | - |
| LiF | .0169 | .0040 | .0002 | - | - |
| $Li_2F_2$ | .0077 | .0021 | .0001 | - | - |
| $Li_3F_3$ | .0012 | .0003 | - | - | - |
| $MnF_2$ | .0005 | - | - | - | - |
| $MnF_3$ | .3236 | .0945 | .0096 | .0018 | - |
| $MnF_4$ | .0006 | .0021 | .0030 | .0026 | .0004 |
| LiF(l) | .0666 | .1734 | .2855 | .4025 | - |
| LiF(s) | - | - | - | - | .5199 |
| $Li_3AlF_6$(l) | .1606 | .1409 | .1105 | .0740 | .0371 |
| $MnF_3$(l) | .2809 | .5154 | .6057 | - | - |
| $MnF_3$(s) | - | - | - | .6204 | .6307 |
| F, $F_2$, $NF_3$, weight percent | .94 | 3.14 | 5.35 | 7.59 | 9.87 |

TABLE B-23. THEORETICAL ANALYSIS OF $LiMnF_5$/Mg

| System No. 2385 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $LiMnF_5$, weight percent | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| Mg, weight percent | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| Combustion parameters | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1727 | 1536 | 1350 | 1219 | 1030 |
| Moles gas/100 g | .282 | .239 | .236 | .258 | .282 |
| Combustion products, moles/100 g | | | | | |
| F | .1635 | .1537 | .0926 | .0530 | .0144 |
| $F_2$ | .0143 | .0680 | .1382 | .2029 | .2671 |
| LiF | .0039 | .0005 | – | – | – |
| $Li_2F_2$ | .0021 | .0004 | – | – | – |
| $Li_3F_3$ | – | .0001 | – | – | – |
| $MnF_3$ | .0953 | .0178 | .0024 | .0003 | – |
| $MnF_4$ | .0024 | .0033 | .0027 | .0013 | .0002 |
| LiF(l) | .5964 | .6106 | .6182 | .6247 | – |
| LiF(s) | – | – | – | – | .6311 |
| $MgF_2$(l) | .2055 | .1321 | – | – | – |
| $MgF_2$(s) | – | .0324 | .1234 | .0822 | .0411 |
| $MnF_3$(l) | .5079 | .5909 | .5065 | – | – |
| $MnF_3$(s) | – | – | .1066 | .6231 | .6309 |
| F, $F_2$, $NF_3$, weight percent | 3.65 | 5.31 | 7.01 | 8.72 | 10.42 |

TABLE B-24. THEORETICAL ANALYSIS OF $LiMnF_5/Mg_3N_2$

| System No. 2322 | 11 | 10 | 9 | 8 | 7 | 6 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|
| $LiMnF_5$, weight percent | 99.50 | 99.40 | 99.30 | 99.20 | 99.10 | 99.00 | 98.90 | 98.80 | 98.70 | 98.60 |
| $Mg_3N_2$, weight percent | .50 | .60 | .70 | .80 | .90 | 1.00 | 1.10 | 1.20 | 1.30 | 1.40 |
| **Combustion parameters** | | | | | | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 797 | 822 | 847 | 872 | 897 | 921 | 944 | 968 | 991 | 1012 |
| $\gamma$ | 1.021 | 1.021 | 1.021 | 1.020 | 1.020 | 1.020 | 1.020 | 1.020 | 1.021 | 1.022 |
| Moles gas/100 g | .298 | .294 | .290 | .286 | .282 | .287 | .275 | .271 | .268 | .266 |
| **Combustion products, moles/100 g** | | | | | | | | | | |
| F | .0009 | .0014 | .0019 | .0026 | .0034 | .0045 | .0058 | .0073 | .0090 | .0109 |
| $F_2$ | .2869 | .2805 | .2739 | .2673 | .2606 | .2539 | .2471 | .2404 | .2339 | .2282 |
| $MnF_3$ | – | – | – | – | – | – | – | – | – | – |
| $MnF_4$ | – | – | – | – | – | – | .0001 | .0001 | .0001 | .0002 |
| $NF_3$ | .0099 | .0119 | .0139 | .0159 | .0178 | .0198 | .0217 | .0235 | .0250 | .0260 |
| $N_2$ | – | – | – | – | – | – | .0001 | .0002 | .0004 | .0009 |
| LiF(l) | – | – | – | – | – | – | – | – | – | – |
| LiF(s) | .6343 | .6336 | .6330 | .6324 | .6317 | .6311 | .6304 | .6298 | .6292 | .6285 |
| $MgF_2$(s) | .0149 | .0178 | .0208 | .0238 | .0267 | .0297 | .0327 | .0357 | .0386 | .0416 |
| $MnF_3$(l) | – | – | – | – | – | – | – | – | – | – |
| $MnF_3$(s) | .6343 | .6336 | .6330 | .6323 | .6317 | .6310 | .6304 | .6297 | .6291 | .6284 |
| F, $F_2$, $NF_3$, weight percent | 11.49 | 11.36 | 11.24 | 11.11 | 10.98 | 10.86 | 10.75 | 10.60 | 10.50 | 10.36 |

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THEORETICAL ANALYSIS OF $LiMnF_5/Mg_3N_2$

| | 6 | 12 | 13 | 14 | 15 | 16 | 5 | 4 | 3 | 2 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 99.00 | 98.90 | 98.80 | 98.70 | 98.60 | 98.50 | 98.00 | 97.00 | 96.00 | 95.00 |
| 0 | 1.00 | 1.10 | 1.20 | 1.30 | 1.40 | 1.50 | 2.00 | 3.00 | 4.00 | 5.00 |
| 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | 921 | 944 | 968 | 991 | 1012 | 1033 | 1121 | 1190 | 1347 | 1358 |
| 0 | 1.020 | 1.020 | 1.020 | 1.021 | 1.022 | 1.024 | 1.000 | 1.028 | 1.031 | 1.030 |
| | .287 | .275 | .271 | .268 | .266 | .265 | .269 | .261 | .278 | .250 |
| 4 | .0045 | .0058 | .0073 | .0090 | .0109 | .0131 | .0273 | .0419 | .0978 | .0877 |
| 6 | .2539 | .2471 | .2404 | .2339 | .2282 | .2234 | .2119 | .1834 | .1343 | .1070 |
| | – | – | – | – | – | – | – | .0002 | .0027 | .0029 |
| | – | .0001 | .0001 | .0001 | .0002 | .0002 | .0005 | .0010 | .0029 | .0026 |
| 8 | .0198 | .0217 | .0235 | .0250 | .0260 | .0262 | .0181 | .0101 | .0017 | .0013 |
| | – | .0001 | .0002 | .0004 | .0009 | .0018 | .0108 | .0246 | .0387 | .0488 |
| | – | – | – | – | – | – | .0103 | .6183 | .6118 | .0054 |
| 7 | .6311 | .6304 | .6298 | .6292 | .6285 | .6279 | .6144 | – | – | – |
| 7 | .0297 | .0327 | .0357 | .0386 | .0416 | .0445 | .0594 | .0891 | .1189 | .1486 |
| | – | – | – | – | – | – | – | – | – | .6001 |
| 7 | .6310 | .6304 | .6297 | .6291 | .6284 | .6277 | .6241 | .6172 | .6063 | – |
| 8 | 10.86 | 10.75 | 10.60 | 10.50 | 10.36 | 10.23 | 9.61 | 8.34 | 7.05 | 5.81 |

TABLE B-25. THEORETICAL ANALYSIS OF $KMnF_5/Mg_3N_2$

| System No. 2344 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $KMnF_5$, weight percent | 95.0 | 96.0 | 97.0 | 98.0 | 99.0 |
| $Mg_3N_2$, weight percent | 5.0 | 4.0 | 3.0 | 2.0 | 1.0 |
| Combustion parameters | | | | | |
| $P_c$, psia | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $T_c$, K | 1350 | 1161 | 1060 | 810 | 483 |
| $\gamma$ | 1.000 | 1.024 | 1.027 | 1.015 | 1.021 |
| Moles gas/100 g | .184 | .175 | .172 | .180 | .222 |
| Combustion products, moles/100 g | | | | | |
| F | .0585 | .0213 | .0098 | .0006 | - |
| $F_2$ | .0710 | .1076 | .1174 | .1400 | .2024 |
| KF | .0004 | - | - | - | - |
| $K_2F_2$ | .0001 | - | - | - | - |
| $MnF_3$ | .0019 | - | - | - | - |
| $MnF_4$ | .0017 | .0005 | .0002 | - | - |
| $NF_3$ | .0011 | .0101 | .0300 | .0396 | .0198 |
| $N_2$ | .0490 | .0341 | .0147 | - | - |
| KF(l) | .5019 | .5078 | - | - | - |
| KF(s) | - | - | .5131 | .5184 | .5237 |
| $MgF_2$(s) | .1486 | .1189 | .0892 | .0594 | .0297 |
| $MnF_3$(l) | .0196 | - | - | - | - |
| $MnF_3$(s) | .4793 | .5073 | .5130 | .5184 | .5237 |
| $F, F_2, NF_3$, weight percent | 3.87 | 5.13 | 6.36 | 7.59 | 8.82 |

## APPENDIX C

## X-RAY ANALYSIS DATA FOR $LiMnF_5$ AND $MnF_4$

All Debye-Scherrer X-ray powder patterns were taken using a 57.3-mm-diameter camera with CuK$\alpha$ radiation and a Ni filter. The d-spacings and intensities are shown in table C-1 for all samples analyzed. All of the samples appeared amorphous rather than crystalline and the manganese tended to cause some interference providing significant background to the resulting patterns.

Comparison of the d-spacings with strong and medium intensities for the first $LiMnF_5$ samples reveals that practically all appear among two or more of the samples analyzed. Preparation No. 14 may be $Li_2MnF_6$ as there is considerable correspondence between the d-spacings of the stronger intensities and those calculated for $Li_2MnF_6$ from the structure determination by Hoppe, et al.[31] The d-spacings for the $MnCl_2$-$BrF_3$ reaction product No. 12 are certainly different than the $Li_2MnF_6$ and $LiMnF_5$ spacings.

TABLE C-1. X-RAY DIFFRACTION POWDER PATTERNS OF $LiMnF_5$ PREPARATIONS

| Line No. | Experimental $LiMnF_5$ No. 1 (Rust) | | Experimental $LiMnF_5$ No. 3 (Gold) | | Experimental $LiMnF_5$ No. 9 | | Experimental $LiMnF_5$ No. 10 | |
|---|---|---|---|---|---|---|---|---|
| | d Spacing | Intensity | d Spacing | Intensity | d Spacing | Intensity | d Spacing | Intensity |
| 1 | 6.2 | s | 6.2 | w | 6.0 | m | 4.3 | vw |
| 2 | 4.7 | w | 4.15 | w | 4.1 | vw | 3.75 | vw |
| 3 | 4.4 | w | 3.80 | s | 3.75 | m | 3.38 | s |
| 4 | 4.1 | w | 3.70 | vw | 3.40 | w | 2.75 | vw |
| 5 | 3.78 | m | 3.45 | m | 3.20 | s | 2.21 | m |
| 6 | 3.41 | m | 3.25 | m | 2.7 | vw | 2.10 | m |
| 7 | 3.20 | m | 2.72 | w | 2.35 | vw | 1.80 | w |
| 8 | 2.75 | vw | 2.38 | w | 2.20 | vw | 1.71 | m |
| 9 | 2.50 | vw | 2.20 | w | 2.10 | s | 1.65 | w |
| 10 | 2.37 | m | 2.10 | m | 2.00 | vw | 1.45 | w |
| 11 | 2.21 | m | 2.00 | — | 1.90 | w | 1.39 | m |
| 12 | 2.10 | m | 1.88 | vw | 1.81 | m | 1.33 | w |
| 13 | 1.90 | w | 1.80 | m | 1.71 | w | 1.20 | vvw |
| 14 | 1.81 | m | 1.70 | vw | 1.64 | m | 0.985 | vvw |
| 15 | 1.69 | w | 1.64 | m | 1.55 | vw | 0.941 | vvw |
| 16 | | | 1.365 | w | | | | |
| 17 | | | 1.275 | w | | | | |

TABLE C-1. (continued)

| Line No. | Experimental $LiMnF_5$ No. 11 | | Experimental $MnF_4$ No. 14 ($MnF_5$) | | Experimental $MnCl_2$ (Alpha Ventron-as received) | | $MnCl_2$ ASTM Index |
|---|---|---|---|---|---|---|---|
| | d Spacing | Intensity | d Spacing | Intensity | d Spacing | Intensity | d Spacing |
| 1 | 5.9 | w | 4.9 | s | 5.85 | s | 5.85 |
| 2 | 4.2 | w | 4.3 | m | 3.15 | w | 3.16 |
| 3 | 3.79 | m | 3.7 | m | | | 3.01 |
| | | | | | 2.95 | vs | 2.99 |
| 4 | 3.41 | s | 3.2 | m+ | 2.58 | s | 2.592 |
| 5 | 3.20 | w | 2.65 | w | 2.37 | vw | 2.371 |
| 6 | 2.65 | w | 2.20 | w | 1.98 | vw | 1.977 |
| 7 | 2.40 | vw | 1.86 | w | 1.85 | m | 1.95 |
| | | | | | | | 1.853 |
| 8 | 2.10 | m | 1.65 | w | 1.81 | vw | 1.812 |
| 9 | 1.81 | m | 1.48 | w | 1.76 | w | 1.766 |
| 10 | 1.72 | w | | | 1.50 | vw | 1.507 |
| 11 | 1.64 | m | | | 1.46 | vw | 1.464 |
| 12 | 1.54 | vvw | | | 1.29 | vw | 1.29 |
| 13 | 1.47 | vvw | | | 1.16 | w | 1.171 |
| 14 | | | | | 1.14 | w | 1.15 |
| 15 | | | | | 1.065 | w | 1.062 |
| 16 | | | | | 0.92 | w | |

Note: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very, very weak.