

Synthesis of Nitrogen Fluorides in a Nitrogen Plasma Jet

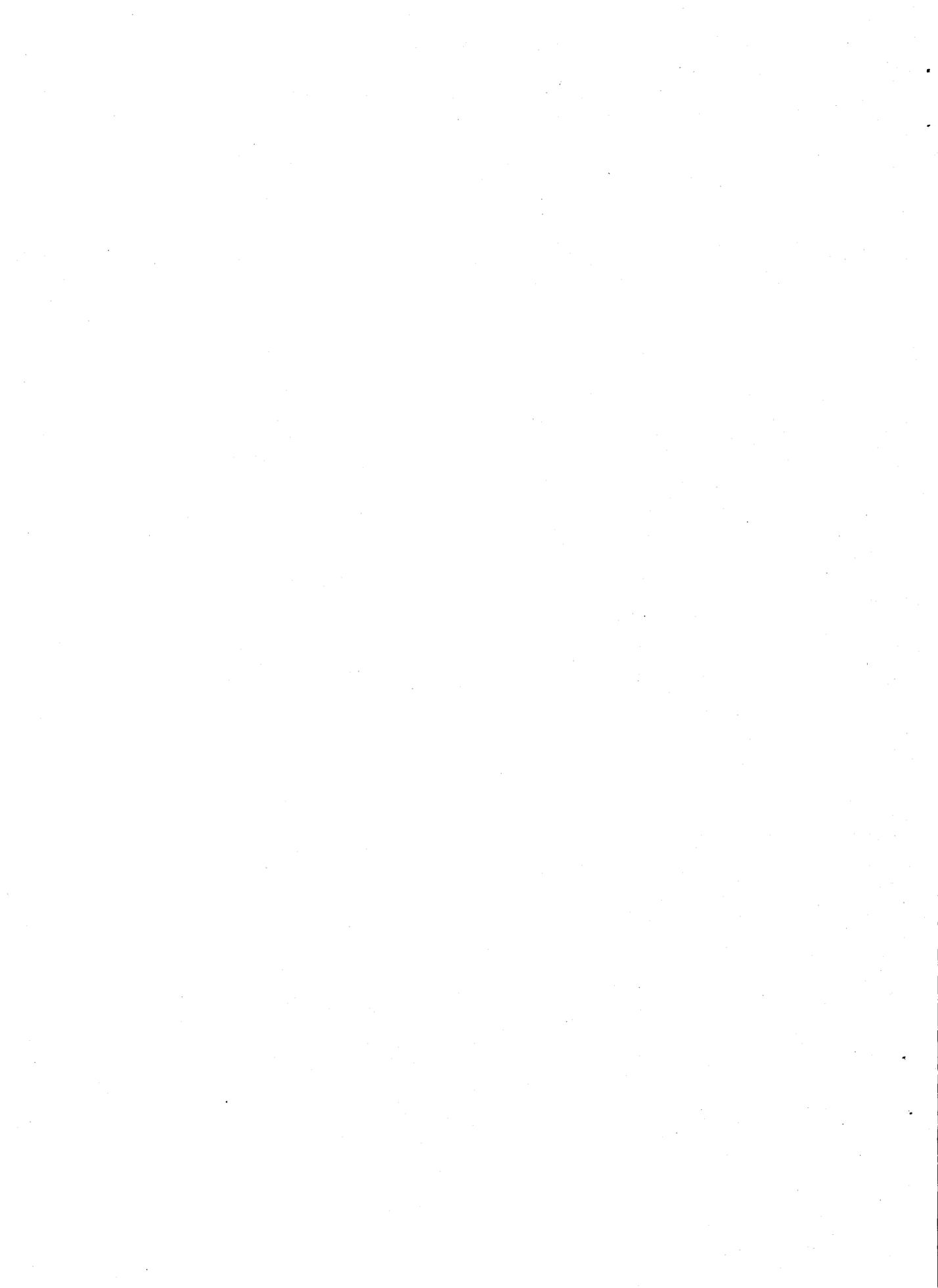
B. R. BRONFIN AND R. N. HAZLETT

*Fuels Branch
Chemistry Division*

January 12, 1966



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.



CONTENTS

Abstract.....	1
Problem Status.....	1
Authorization.....	1
INTRODUCTION	1
THE PLASMA ARC REACTION PROCESS.....	2
Plasma Generator.....	2
Intermixing of Reagent	2
Quench	2
EXPERIMENTAL APPARATUS AND OPERATION.....	3
Description	3
Range of Variables.....	4
Product Analysis	4
Characteristics of the Nitrogen Plasma Jet.....	4
THERMOCHEMICAL CALCULATIONS FOR THE MIXED PLASMA	4
Calculations for the C-N-F System.....	5
Energy Balance.....	6
QUENCH PRODUCTS AND REACTIONS	6
Composition.....	6
Reaction Paths	7
Related Studies	8
Effect of Power and F/N Ratio on Yields.....	8
SULFUR HEXAFLUORIDE AS A FLUORINE CARRIER.....	9
ANALYSIS OF RESULTS BASED ON THERMOCHEMICAL EQUILIBRIUM.....	10
SUMMARY	11
REFERENCES	11



Synthesis of Nitrogen Fluorides in a Nitrogen Plasma Jet

B. R. BRONFIN AND R. N. HAZLETT

*Fuels Branch
Chemistry Division*

Nitrogen-fluorine compounds have a high energy content, which makes them of interest in the propellant field. An electric arc technique, which has been used in the synthesis of other high-energy compounds, has now been applied to the nitrogen-fluorine system. A nitrogen plasma jet was intermixed with gaseous fluorides (CF_4 or SF_6) and subsequently quenched. Small yields of NF_3 , N_2F_4 , and CF_3NF_2 were produced, together with trace quantities of other products.

The observed products have been accounted for by a reaction sequence involving the formation of FCN and its subsequent stepwise fluorination by addition at the triple bond. FCN is only an intermediate, however, and has not been found in the product stream.

The yield of fixed-nitrogen products is about 1% of inlet nitrogen for typical conditions, and it increases with increasing power input and increasing F/N ratio in the plasma.

INTRODUCTION

The advantages to be gained from the use of rocket propellants of higher energy content has stimulated extensive research into new compounds for use as fuels or oxidizers and new synthesis techniques for formation of high-energy-content compounds. Nitrogen-fluorine compounds are among the high-energy compounds of interest, and some of the new techniques have been used for the synthesis of these compounds.

The use of nitrogen trifluoride, NF_3 , and tetrafluorohydrazine, N_2F_4 , as liquid rocket oxidizers has been discussed briefly by Haberman (1) and in more detail in the classified literature. There has been additional interest in solid rocket propellants containing nitrogen-fluorine bonds (2).

The following compounds composed of nitrogen and fluorine have been studied and reported: nitrogen trifluoride, NF_3 (3); fluorine azide FN_3 (4); *cis*- and *trans*-difluorodiazine, N_2F_2 (5); and tetrafluorohydrazine, N_2F_4 (6). All of these compounds are stable at room temperature with the exception of fluorine azide, which readily decomposes to N_2F_2 .

Bigelow and his co-workers (7-9) have investigated organic compounds containing nitrogen and fluorine. Dresdner and others (10-11) have contributed additional research in this area. Glemser and co-workers (12) and Logothetis

et al. (13) have investigated sulfur compounds containing nitrogen and fluorine. A good deal of the nitrogen-fluorine work has been reviewed by Hoffman and Neville (2). All of the synthesis reported have been carried out under conventional conditions, at temperatures less than 600°C.

Recently a number of interesting chemical syntheses have been carried out in an electric arc, a high-energy technique. A partially ionized gas zone, or plasma, is established and electrical energy pumped in, to achieve very high temperatures. Temperatures from 2000 to 20,000°K have been exploited for chemical synthesis in plasma arc reactors. At these arc temperatures reaction rates are extremely rapid. This high-temperature, high-energy regime appeared applicable to the synthesis of nitrogen-fluorine compounds.

A group of studies using the high-intensity carbon arc for chemical synthesis have been carried out at Massachusetts Institute of Technology. Acetylene, C_2H_2 , was successfully produced from the reaction of hydrogen or methane with the carbon arc (14). Tetrafluoroethylene, C_2F_4 , was produced from the reaction of carbon tetrafluoride with the carbon arc (15). Recent work by Freeman (16) utilized the nitrogen plasma jet intermixed with methane to produce hydrogen cyanide, HCN.

Some work in high-temperature N-F synthesis has been briefly described in a U.S. Patent (17). Nitric oxide was reacted with CF_4 in the vicinity of a carbon arc, but the yields of fixed nitrogen, as NF_3 , were low and the power consumption high.

NRL Problem C01-05 and Project RR 010-01-44-5851. This is a final report on this phase of the problem. Manuscript submitted August 10, 1965.

In the present study a nitrogen plasma jet was intermixed with gaseous fluorides, CF_4 and SF_6 . These relatively inert gaseous fluorides are convenient carriers to introduce fluorine into the laboratory reactor. A rapid quench was provided downstream and complete analysis of the quenched product gases was made. High power input, rapid reagent mixing, and rapid quenching were incorporated into a simple plasma jet reactor to maximize the production of nitrogen fluorides at minimum unit power consumption.

THE PLASMA ARC REACTION PROCESS

The process of chemical synthesis *via* the plasma arc can be examined as three separate steps occurring in times on the order of milliseconds, as diagrammed in Fig. 1.

Plasma Generator

Cold reactant gas A, which in this study was exclusively dry nitrogen, is fed to the plasma generator. Many generators have been described in the literature (18,19). In the present experiments one of the commercially available plasma jets (20) was used. A dc arc is established, powered by a 35-kw supply, to form a luminous, steady, high-temperature jet of nitrogen plasma. Available temperatures from 2000 to 15,000°K are a function of power input, composition of the

plasma-forming gas, and design of the plasma generator.

Intermixing of Reagent

To promote chemical combination, reactant gas B is intermixed with the hot plasma in the second step. Frequently, as in these experiments, it is necessary to introduce a reactant downstream from the plasma generator, as shown. This is essential if the heated reactant gas is likely to be corrosive to the metal electrodes of the generator. In this study the B gas was carbon tetrafluoride, CF_4 , or sulfur hexafluoride, SF_6 . As a consequence of the introduction of cold reactant gas, marked chilling takes place, and the gas mixture may typically cool to 1500 to 4000°K. The extent of cooling is a function of the heat capacity of the reactant gases and the ratio of gas flow rates, A/B. If good gas mixing is accomplished and sufficient enthalpy is carried out of the plasma generator, a high temperature level can be sustained in the multicomponent plasma mixture. The high temperature will allow the formation of high concentrations of free radicals and reactive intermediates, which will serve as precursors to the desired products.

Quench

Since a gradual cooling of the labile intermediates formed in the mixing step will not

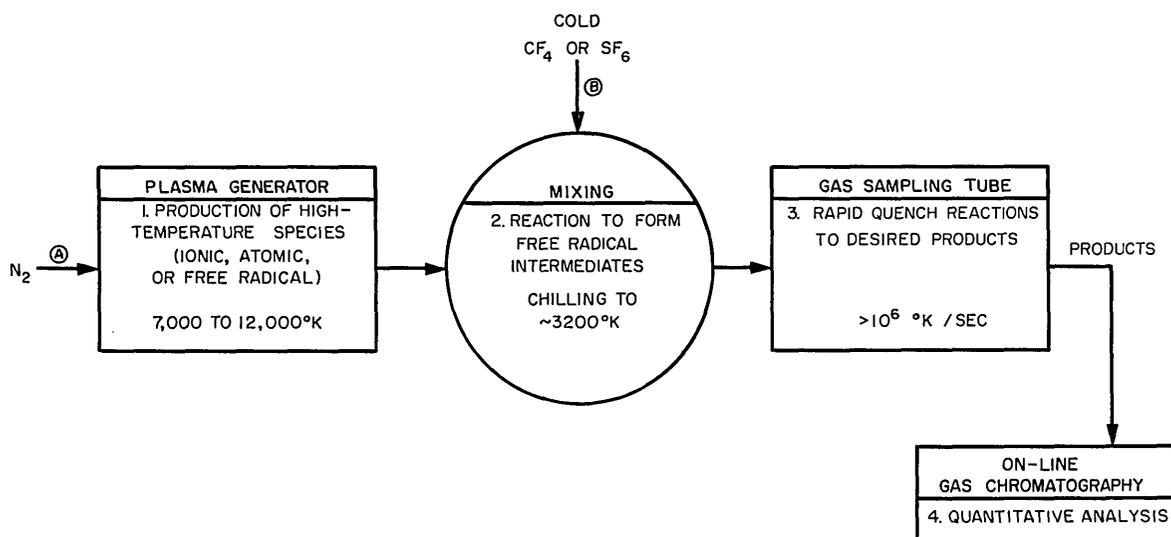


Fig. 1 — The plasma arc reaction process

always yield the most interesting or valuable products and may well allow the system to revert to the original reactants; a quenching step is necessary. In these experiments a small-diameter (0.032 in. I.D.), water-cooled, stainless steel tube, through which a continuous gas stream could be withdrawn, was employed. The quenching rate is estimated to be in excess of 10^6 °K/sec (21-23). In selecting a quenching device, one must consider whether the introduction of additional species into the plasma mixture during quench would be desirable. Some techniques, which quench by entrainment of cold fluid, add new species to the plasma. The quench tube, as used in these experiments, avoids this complication. Within the cold quench tube the precursor species react to yield the observed product distributions. The quench tube is itself a reactor.

EXPERIMENTAL APPARATUS AND OPERATION

Description

Figure 2 shows a diagram of the normal configuration of the plasma jet reactor. The plasma generator, supplied by a 35-kw dc power supply, is shown as a thoriated tungsten cathode separated by a small gap, for passage of the nitrogen feed, from a copper anode nozzle. The nozzle diameter is 5/16 in. I.D. The small-diameter (0.046 in. I.D.) gas injection ports, which are set normal to the mainstream flow, are indicated at a position 1/8 in. downstream from the nozzle.

The operating plasma jet was fired into a water-cooled reactor of ~ 0.1 cu ft volume which was sealed to exclude air. Viewing ports were provided on the reactor for visual alignment and positioning of the probe and for observation of the plasma jet. In the experimental procedure, the reactor was purged with dry nitrogen at 100 standard cu ft/hr (SCFH) for a minimum of 1 min. After the arc was initiated and operated on pure nitrogen for a few seconds, gaseous fluoride feed was added to the plasma. Current and voltage, which were continuously recorded on a dual-channel strip-chart recorder, were adjusted to the desired value. Arc operation was stabilized for at least 15 sec before a sample was taken for gas analysis.

Cooling-water flow rate through the plasma generator was monitored with a calibrated rotameter. Interconsistent mercury thermometers, calibrated in tenths of a degree Centigrade, were placed into the inlet and exit of the cooling-water lines feeding the plasma generator. Thus enthalpy lost to the cooling water could be determined and then subtracted from the electrical power input to establish the net enthalpy of the gas stream leaving the plasma jet head. The additional heat losses downstream, into the reactor cooling lines and the gas sampling probe cooling water were not considered. This enthalpy instrumentation was added after much of the data had been collected and was not available for all runs.

The gas-sampling probe, diagrammed in Fig. 2, consists of three concentric tubes with an overall

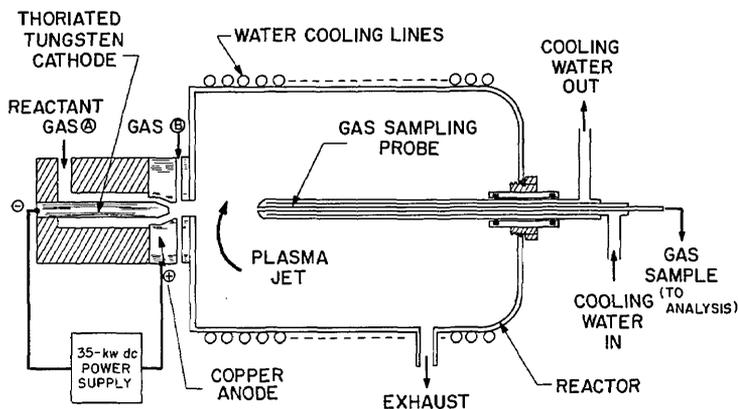


Fig. 2 - Plasma jet reactor

diameter of 3/8 in. O.D. Thus the probe diameter is of the order of the plasma jet diameter. Normally, the tip of the probe was placed directly into the luminous plasma zone, with the entrance of the quenching tube 1/4 in. from the effluent of the jet from the anode nozzle. This separation distance is approximately equal to one nozzle diameter. This close position minimizes the entrainment of ambient gas into the plasma mixture before quench within the cold quench tube. A sliding vacuum seal allowed variable location of the probe tip along the central axis of the reactor when desired. The metal probe is protected from melting by a high flow rate of cooling water sent into the probe at 160 psig.

Range of Variables

The flow conditions and nozzle geometry for the plasma generator were selected to create a turbulent, subsonic jet for all runs. Pressure in the reactor chamber, into which the plasma jet exhausts, was held at 1 atm for most of the data runs. A few additional experiments were performed at pressures down to 100 mm Hg. The nitrogen feed rate through the plasma generator was fixed at 100 SCFH (79 cc/sec at S.T.P.) for most runs, although a range from 50 to 100 SCFH was also studied. Gaseous fluoride feed rate was varied from 0 to 100 SCFH, using either CF_4 or SF_6 . Power input levels were varied from 5 to 25 kw.

Product Analysis

The quenched gas stream was sent to on-line gas chromatography for analysis. Gas chromatogram peaks were identified by mass spectroscopy and then calibrated with pure samples.

Characteristics of the Nitrogen Plasma Jet

Actual temperature measurements of neither the pure nitrogen nor the mixed nitrogen-fluorine plasmas were made in these experiments. No direct experimental attempt was made to identify the species present in the luminous plasma. Jahn (24) has spectroscopically determined the temperature profile of the pure nitrogen plasma jet, under similar flow and power input conditions. Steep radial temperature gradients, on the order of $1000^\circ\text{K}/\text{mm}$, were observed.

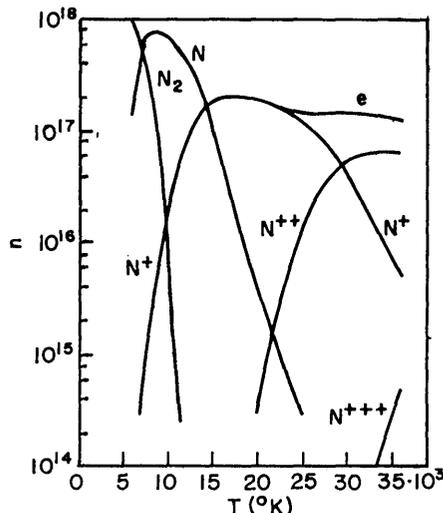


Fig. 3 — Equilibrium concentration in nitrogen plasma

Although the plasma jet is not isothermal, the assumption of local thermodynamic equilibrium can be made. It is informative to calculate the composition of a nitrogen plasma as a function of temperature, based on known thermodynamic data. Figure 3 (25,26) shows that at 8000 to $12,000^\circ\text{K}$, which would include the expected temperatures of the plasma jet leaving the generator head, the plasma is mainly nitrogen atoms, N . The nitrogen ion N^+ becomes an important species above $12,000^\circ\text{K}$. In the cooler range; below 7000°K , the equilibrium shifts to predominantly diatomic nitrogen molecules N_2 .

THERMOCHEMICAL CALCULATIONS FOR THE MIXED PLASMA

Into the high-specific-enthalpy nitrogen plasma a cold gaseous fluoride was introduced. Based on the thermochemical data in the literature (27), and using a computer program employing a free-energy minimization technique (28,29), the theoretical compositions for the resulting plasma mixtures at chemical equilibrium can be calculated as a function of temperature. While many of the presently available thermodynamic properties of these high-temperature species are the result of extrapolation and other estimation techniques, the equilibrium composition diagram can serve as a very useful guide.

Calculations for the C-N-F System

Figure 4 shows the equilibrium composition of a C-N-F mixture in the atomic ratio of 1:4:4, corresponding to a feed ratio CF_4/N_2 of 1/2. The y axis carries mole fraction of the different species ranging from 0.0001 to 1.0, for 1 atm total pressure; the x axis carries the temperature from about 2500 to 6000°K. The predominant species over the entire range is atomic fluorine. Next in concentration is the inactive nitrogen molecule. In the lower half of the temperature range the

C-F series is found, with CF_2 appearing as the most stable fragment. CF_3 and CF are at lower concentrations. C_2F_2 , difluoroacetylene, is stable over a fairly broad range, about 3000 to 4000°K. Difluoroacetylene has recently been reported to be successfully synthesized at 10 to 20 mm Hg pressure but to be very reactive at room temperature (30,31). Experimental evidence for its presence at these temperatures in the large concentrations predicted from the estimation of its thermochemical properties is unconfirmed, however. Around 4500°K the equilibrium shifts away

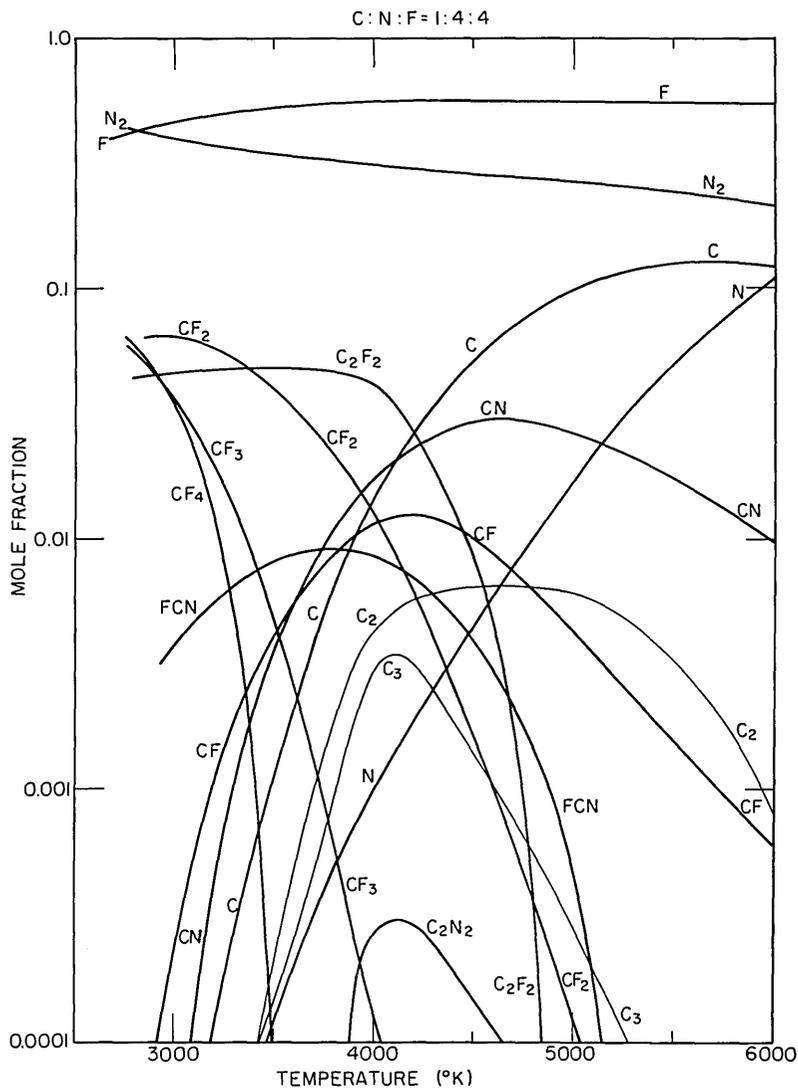


Fig. 4 - Carbon-nitrogen-fluorine system equilibrium calculations at 1 atm

from C-F compounds to free carbon compounds. In this system atomic carbon is in high concentration at high temperatures; the lower concentrations of the C₂ and C₃ forms are also shown on the diagram.

At temperatures not much above 7000°K, the system is reduced to its atomic constituents, F, C, and N. There are two bonded-nitrogen compounds at significant concentrations: CN, a free radical which is stable between 4000 and 5500°K, and FCN, fluorocyanogen, a known compound (2) which is calculated to be present at about 1 mole-% in the range of 2500 to 4500°K. Several other species (including NF and NF₂, for instance) are not shown on Fig. 4 because their calculated mole fraction is less than 10⁻⁴. These were considered, nevertheless, in the calculation of the equilibrium composition.

Energy Balance

To determine the distribution of species corresponding to conditions in the mixed plasma, an estimate of the plasma temperature is needed. Knowing the power input, heat loss to the cooling water, and the feed rates of N₂ and CF₄, the mean enthalpy of the plasma mixture can be established by energy balance. Since the heat capacity data are known (27), the average temperature of the plasma mixture as it leaves the plasma generator can be calculated. This calculation is included in the computer program output. For a typical experimental condition (N₂ feed at 100 SCFH, CF₄ feed at 50 SCFH, and a 20-kw power input) there is a 68% efficiency in electrical energy transfer to the plasma. This efficiency remains almost constant over the range of variables covered in these experiments (see Experimental Apparatus and Operation section) and is in reasonable agreement with other studies (24,32). The heat loss to the cooling water is mainly a function of the particular geometry and spacing of the cathode and anode of the plasma generator. For these typical conditions, then, the net average enthalpy of the plasma mixture is calculated to be 1.36 kcal/g, corresponding to a temperature of 3600°K. At this temperature the ratio of bonded nitrogen, as FCN, to molecular nitrogen, N₂, is about 0.02.

In relating such theoretical calculations, based upon an isothermal mixture at a given temperature, to the plasma jet experiment, one should

consider that the mixed plasma jet is likely to maintain the nonisothermal profile of the issuing jet. Grey and Jacobs (33) have studied the mixing of cold helium with an argon plasma jet. Radial temperature gradients on the order of 500°K/mm persisted about two nozzle diameters downstream from the nozzle. Similar gradients were observed in the degree of mixing, which is only partially complete about two diameters downstream from the nozzle. Both the concentration and temperature profiles become essentially flat at four diameters downstream from the nozzle under typical conditions. At this distance, however, temperatures decay to low values which are detrimental to fixed nitrogen yields. Thus, conditions at the quench tube entrance, when located at 1/4 in. (one nozzle diameter) from the plasma jet nozzle, are rather poorly defined.

QUENCH PRODUCTS AND REACTIONS

The question now to be asked is what would be the result of quenching the plasma mixture from about 3500°K to room temperature in less than a millisecond. The quenching probe performs this rapid cooling (21,23). Giving consideration to the chemical stability of the transient species, it could be expected that some would be preserved upon quenching, *e.g.*, N₂, but that others would undergo reaction with the 50 mole-% concentration of atomic fluorine in the quenching process.

Composition

The observed distribution of compounds in quenched gas stream is distinctly different from the postulated equilibrium composition of the high-temperature plasma. Figure 5 shows the analysis of the quench of a plasma formed with a 19-kw total power input, N₂ feed rate of 75 SCFH (0.026 g-mole/sec), and CF₄ feed rate of 15 SCFH (0.005 g-mole/sec) at 1 atm pressure. Product yield is expressed, on the y-axis, as the ratio of the effluent flow rate of a particular product, \dot{x} , to the nitrogen feed rate entering the plasma generator, \dot{N}_2 . Focusing attention on the distribution observed when the quench probe tip was located 1/4 in. from the anode nozzle, it is observed that the total bonded nitrogen is about 1%. Perfluoromethylamine, CF₃NF₂, a known

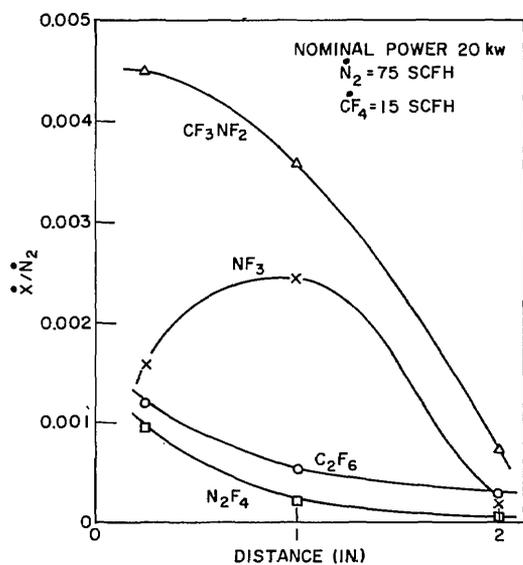


Fig. 5 - Variation of product distribution with location of probe intake position

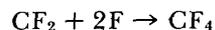
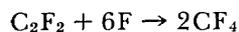
compound (2), is the major constituent. Nitrogen trifluoride, NF_3 , hexafluoroethane, C_2F_6 , and tetrafluorohydrazine, N_2F_4 , are also present. Trace quantities of difluorodiazine, N_2F_2 , (*cis* and *trans* isomers occur in equal concentration) and tetrafluoroethylene, C_2F_4 , are observed. Trace components were difficult to determine following the normal experimental procedure of sampling directly from the continuous product stream into a gas chromatograph. However, the product stream from the quench probe was, on occasion, sent through a liquid-nitrogen trap. Subsequent gas chromatographic analysis of the condensed products allowed easy determination of all components. The fixed-nitrogen components account for almost 1% of the product stream, the remainder being nitrogen and carbon tetrafluoride in approximately the same ratio as the feed. No carbon deposit was noted on the interior of the reactor or quench probe. A very thin, light-colored coating was observed on the surface of the probe; it was probably a metal fluoride.

A set of preliminary data, Fig. 5, shows the variation in quenched gas composition as the probe tip is moved away from the plasma nozzle. The main effect is a gradual reduction in the total yield of fixed-nitrogen products. Note that the yield curves for N_2F_4 and C_2F_6 follow each other

quite closely and are nearly equal. Two physical effects are present as the separation between plasma jet nozzle and quench tubes increases: (a) The quench tube sample gas from successively cooler plasma regions. Grey and Jacobs (33) have noted a typical temperature decay of $2000^\circ K$ per axial length equal to a nozzle diameter. (b) More time is available for gas diffusion and mixing, including the entrainment of the ambient nitrogen which initially fills the reactor. This dilution has the effect of decreasing measured yield.

Reaction Paths

The fact that most of the carbon and fluorine is found in the product stream as CF_4 can be explained as a result of the fluorination of the labile C-F species predicted in the high-temperature plasma at equilibrium. Major constituents seen in Fig. 4 would be subject to fluorination by the excess of atomic fluorine to yield the very stable carbon tetrafluoride:



etc.

Additional amounts of CF_4 could be the result of incomplete mixing or channeling directly from feed port to quench tube entrance.

The bonded-nitrogen species, FCN, also would be subject to fluorine attack during quench. Figure 6 postulates a mechanism to account for the observed product distribution formed from fluorocyanogen as the precursor. A handicap for researchers in the field of plasma chemistry is the absence of kinetic data in the range of plasma temperatures for all but a few chemical systems. Thus the quench kinetics and reaction path must be only tentatively stated. The quench reactions are likely a sequential fluorination of the plasma species, with some side dimerization reactions. From the high-temperature equilibrium species, FCN, direct fluorine addition would yield trifluoromethylenimine, CF_2NF . Neither FCN or CF_2NF have been identified in the product stream. The known chemical properties of FCN (34) and of CF_2NF (35) suggest them to be less stable than

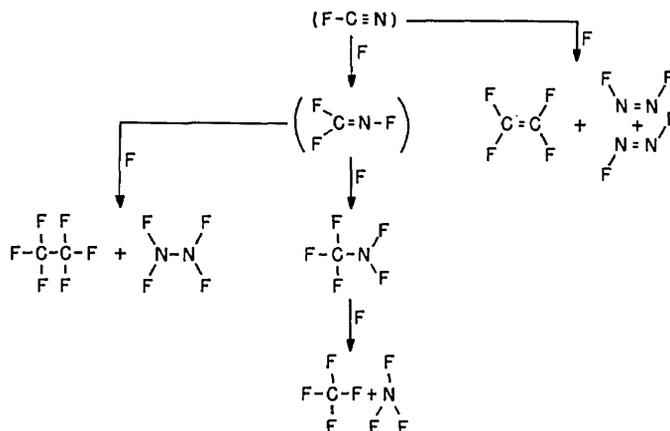


Fig. 6 — Fluorination during quench

the other nitrofluorocarbon and nitrogen fluoride compounds considered here. If, during the first fluorination step, the C-N bond is ruptured and dimerization occurs, the side reaction to difluorodiazine and tetrafluoroethylene would result. The equilibrium ratio of the *cis* to *trans* isomers of N_2F_2 is reported equal to 7:1, established at 285°C (36). As mentioned above, however, equal amounts of the *cis* and *trans* forms are observed, although in trace concentrations. This departure from equilibrium gives further evidence to the rapid quench rate provided by the probe. The statement of formation of C_2F_4 exclusively *via* this step cannot be fully justified, since C_2F_4 could be a reaction product of direct fluorination of one of the carbon-fluorine fragments. Since both the C_2F_4 and N_2F_2 concentrations were at trace level, full correlation between the two concentrations was not made in these experiments.

In the second fluorination step the major product component, CF_3NF_2 , is formed. The larger concentration of CF_3NF_2 , in relation to other products, is explained by the conversion of the less stable CF_2NF to the fully fluorinated CF_3NF_2 . The side reaction, wherein the C-N bond is not preserved upon fluorination, forms hexafluoroethylene, C_2F_6 , and tetrafluorohydrazine, N_2F_4 , by dimerization of the fragments. The nearly equal amounts of these two symmetric products, under a variety of conditions, as was seen in Fig. 5, add credence to this postulated step. Finally, with complete fluorination nitrogen trifluoride, NF_3 , and carbon tetrafluoride, CF_4 , are formed.

In all of the above steps the cold wall of the quench tube serves to carry away the heat of reaction. Some additional experiments with smaller probes, 0.012 in. I.D. and 0.006 in. I.D., showed no significant variations in product composition. The effect of different materials of construction for the inner quench tube wall has not been explored.

Related Studies

A substantial amount of research in C-N-F compounds has been done in more conventional environments, not employing the plasma arc. The formation of cyanogen fluoride from cyanuric fluoride and its decomposition at moderately high temperatures ($\sim 2000^\circ K$) and at about 50 mm pressure have been briefly described. In those studies, CF_4 , C_2F_4 , and NF_3 were among the important products and decomposition products (34,17). Bigelow and his co-workers (7,8) have carried out direct fluorinations of nitrogen-substituted hydrocarbons at conventional temperatures ($\sim 150^\circ C$). By adjusting reactor conditions they have produced a mixture of nitrofluorocarbons, including F_2CNF , F_3CNF_2 , and NF_3 . FCN has been postulated as an intermediate in these reactions (9).

Effect of Power and F/N Ratio on Yields

The overall effect of an increase in the power input and a variation of the C:N:F ratio in the plasma is seen in Fig. 7. The concentration of

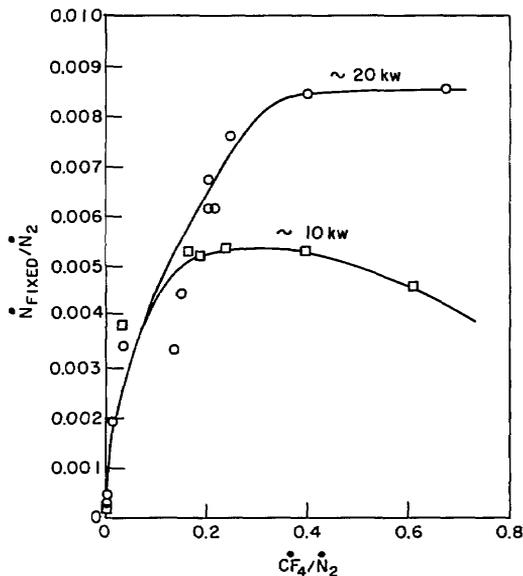


Fig. 7 - Ratio of fixed nitrogen to inlet nitrogen flow rate versus ratio of fluoride feed to inlet nitrogen flow rate. Curves are identified with nominal power inputs.

fixed nitrogen occurring in the different product species has been lumped together as \dot{N}_{fixed} . The ratio of \dot{N}_{fixed} to \dot{N}_2 , the inlet nitrogen feed rate, appears on the y axis. The ratio of feed rates, $\dot{C}F_4/\dot{N}_2$, is presented on the x axis.

Data for the plot were taken with the tip of the quench probe about one nozzle diameter ($1/4 \pm 1/8$ in.) from the head of the plasma generator. The product distribution for these runs remained in approximately the same ratio as shown on Fig. 5 for $d = 1/4$ in. The nitrogen feed was fixed at 100 SCFH (0.035 g-mole/sec) for this series of runs. The points are grouped about two nominal power input levels, 10 kw and 20 kw. Actual power input values with less than a 5% deviation from 10 kw were plotted as 10 kw; likewise, for 20 kw. As mentioned in the Experimental Apparatus and Operation section, approximately 70% efficiency is attained in operation, so the net power delivered to the plasma would be 7 kw and 14 kw, respectively, for these data.

There is a definite increase in yield as more power is coupled into the plasma. This is particularly apparent at the higher $\dot{C}F_4/\dot{N}_2$ ratios. The peak product yield at the higher power level is almost twice the peak yield at the lower power level. Part of the scatter in the data is due to

variations in the percentage of power lost to the cooling water from the plasma. Variations of $\pm 5\%$ were typical but were not measured for each run. A second possible source of scatter is due to inexact positioning of the probe on the centerline of the jet. This would allow intake of some cool plasma outside the hot core.

In the low-power runs, the yield of nitrogen fluorides initially increased as additional fluorine, as CF_4 , was introduced into the plasma. However, the yield turned downward as the flow rate of cold fluoride reagent further increased. The same effect of a diminishing gain in yield with increasing reagent flow rate was noted in the high-power runs. If the high-power curve were extended, a similar decreasing segment might be expected at $\dot{C}F_4/\dot{N}_2$ ratios much greater than 1.

The effect of reactor chamber pressure was examined in a few experiments. No significant changes in yield were noted in reducing the pressure from 760 to 100 mm Hg.

SULFUR HEXAFLUORIDE AS A FLUORINE CARRIER

A series of runs was made with sulfur hexafluoride, SF_6 , substituted for carbon tetrafluoride, CF_4 , as the reagent. Similar results were found, as shown in Fig. 8. In the S-N-F case the only bonded-nitrogen compound observed in the product stream was NF_3 . Had small quantities of N_2F_4 been present, its detection would have been obscured by the large SF_6 peak in gas chromatographic analysis. Other trace constituents in the quenched gas stream were identified by mass spectroscopy as fluorocarbon contaminants, CF_4 and CF_3NF_2 . Carbon was apparently introduced into the system through fluorine attack on O-rings or on deposits remaining after CF_4 runs. Some solid sulfide formation was observed on the metal surfaces of the probe. For the sulfur system the total concentration of bonded nitrogen is about the same as in the previous runs with CF_4 , near 1%. The similar maximum yield behavior with increasing F/N ratios is found, as seen in Fig. 8.

Stable operation of the plasma jet was experienced at both power levels over the full range of F/N feed ratios. A substantial reduction in the luminosity of the plasma occurred as increasing quantities of fluoride reagent were injected.

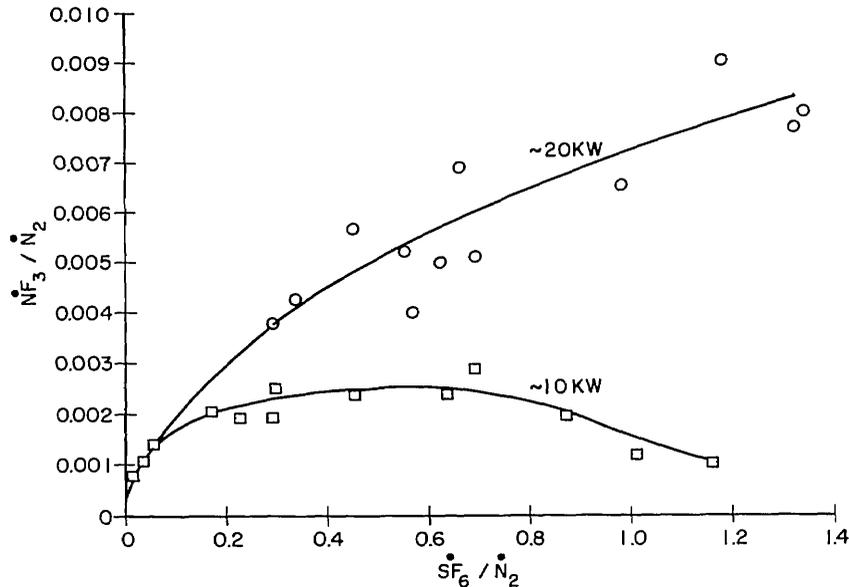


Fig. 8 — Ratio of NF_3 in product to inlet nitrogen flow rate versus ratio of fluoride feed to inlet nitrogen flow rate. Curves are identified with nominal power inputs.

A theoretical analysis of the equilibrium of the mixed S-N-F plasma was not made because of the inadequacy of thermochemical data for the S-F, S-N, and mixed S-N-F species at plasma temperatures.

ANALYSIS OF RESULTS BASED ON THERMOCHEMICAL EQUILIBRIUM

The variation in yields graphed in Figs. 7 and 8 are the result of the two following effects, which are qualitatively illustrated in Fig. 9.

1. Referring to the equilibrium diagram in Fig. 4, the concentration of bonded-nitrogen species, as FCN, increases with increasing temperature between 1500 and 3700°K, and at higher temperatures as CN. Thus, equilibrium predicts that as the specific enthalpy is increased, bringing about an increase in the plasma temperature, the concentration of N-F product precursors would increase. This phenomenon creates the higher yields which are observed at higher power input levels.

2. A series of equilibrium calculations has been made at differing C:F:N ratios, in addition to that for the one ratio diagrammed in Fig. 4. These calculations, not presented here, show that at a given temperature the equilibrium

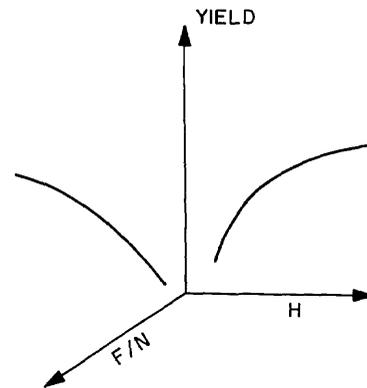


Fig. 9 — Yield as a function of plasma enthalpy level, H, and fluorine-to-nitrogen ratio, F/N

concentration of N-F precursors also increases with increasing ratios of F/N. The initially increasing yields of N-F products at fixed power levels shown in Figs. 7 and 8, in the region where the ratio of fluoride to nitrogen feeds is increasing from 0 to about 0.5, is explained by this equilibrium shift. Maya (37) has found evidence of this effect, under very different conditions.

The increasing addition of cold fluoride, while effecting a shift in equilibrium toward higher yields, is also chilling the plasma mixture in the

experimental system. This produces a lower specific enthalpy of the plasma and reverses the upward shift in equilibrium by lowering the plasma temperature. Thus, the increasing, then leveling, then decreasing yield plot (Figs. 7 and 8) can be explained as, first, the contribution of the F/N ratio increase, next the balancing of F/N ratio increase with the mixed plasma enthalpy decrease, and last, the predominance of chilling of the plasma by cold reagent feed. The full range of these effects is more obvious at low enthalpy than at the high enthalpy levels established with higher power input.

A correlation of these experimentally obtained plots with a theoretical analysis of the thermochemical data was attempted for the C-F-N system. For the theoretical calculation, one needs to know the composition of the plasma, in terms of the ratio N:C:F. While the bulk flow rates of N₂ and CF₄ are known, the mixing of cold CF₄ with the nitrogen plasma may be incomplete at the entrance to the quench tube. Thus a mass balance is not well established. With the steep radial temperature gradient of the plasma jet considered, one is not sure of the enthalpy level of that portion of the plasma being sampled by the quench tube. Thus an energy balance is not well established. When a fully mixed, isothermal model is used, the correlation between experimental yield and thermodynamic equilibrium yield as a function of CF₄/N₂ ratio and net power is poor. However, the experimental yield of fixed nitrogen never exceeds the highest theoretical prediction of fixed nitrogen precursor (as FCN), which occurs at about 3800°K on the thermochemical equilibrium plots. A precise theoretical analysis would require some modifications to the experimental design to obviate the complexities in establishing the mass and energy balance in the plasma jet system.

The results of this plasma synthesis appear to be satisfactorily explained by a consideration of the equilibrium of the mixed plasma. Corollary supporting evidence is available from the C-N-H system. Equilibrium calculations predict that HCN would be a significant product over a wide enthalpy range. This has been observed in plasma experiments by Freeman (16) and at NRL. Freeman has postulated that the HCN precursor is a long-lived, charged nitrogen species which is present in concentrations up to 12%, the

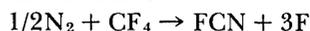
maximum HCN concentration found in the product stream. Since 1% yields of N-F products were found in the CF₄/N₂ system, utilizing the same nitrogen plasma which affords 10% HCN in the CH₄/N₂ system, it is suggested that the equilibrium thesis explains the results more consistently.

The study of quenching kinetics in these high-temperature ranges and at these accelerated cooling rates is just beginning (23). It is uncertain where in the quenching path, or even possibly in the mixing path, the equilibrium of these high-temperature species may be frozen.

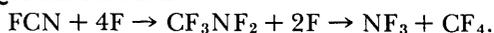
SUMMARY

The reaction of a nitrogen thermal plasma with gaseous fluorides has been observed to produce a variety of N-F compounds upon quenching. Consideration of the thermochemical equilibrium for the N₂ + CF₄ plasma reaction in conjunction with the experimental results suggests the following primary reaction path:

Plasma reaction:



Quench reaction:



Additional side reactions are also observed. NF₃ is also formed in the N₂ + SF₆ plasma reaction.

The yield of fixed-nitrogen products is about 1% of inlet nitrogen for typical conditions, corresponding to a rate of NF₃ production equal to 0.01 lb/kw-hr. The yield increases with increasing power input, which effects an increase in temperature. The yield also increases with increasing F/N ratio in the plasma. For the range of conditions covered, equilibrium predicts that nitrogen fluoride precursors are favored at conditions of high temperature and excess fluorine.

A complete correlation between the thermodynamic equilibrium prediction of yield and experimental data is complicated by an incomplete determination of energy balance and stoichiometry within the plasma jet.

REFERENCES

1. Haberman, E.G., *Chem. Eng. Prog.* **60**(No. 7):72-76 (1964)
2. Hoffman, C.J., and Neville, R.G., *Chem. Rev.* **62**:1-18 (1962)

3. Ruff, O., Fischer, J., and Luft, F., *Z. Anorg. Allgem. Chem.* **172**:417 (1928)
4. Haller, J.F., Ph.D. Dissertation, Cornell Univ., Ithaca, N.Y., Sept. 1942
5. Bauer, S.H., *J. Am. Chem. Soc.* **69**:3104 (1947)
6. Colburn, C.B., and Kennedy, A., *J. Am. Chem. Soc.* **80**:5004 (1958)
7. Cuculo, J.A., Bigelow, L.A., *J. Am. Chem. Soc.* **74**:710-713 (1952)
8. Gervasi, J.A., Brown, M., and Bigelow, L.A., *J. Am. Chem. Soc.* **78**:1679-1682 (1956)
9. Robson, P., McLoughlin, V.C.R., Hynes, J.B., and Bigelow, L.A., *J. Am. Chem. Soc.* **83**:5010-5015 (1961)
10. Dresdner, R.D., Tlumac, F.N., and Young, J.A., *J. Am. Chem. Soc.* **82**:5831 (1960)
11. Young, J.A., Durrell, W.S., and Dresdner, R.D., *J. Am. Chem. Soc.* **81**:1587 (1959); **82**:4553 (1960)
12. a. Glemser, O., Schröder, H., and Haeseler, H., *Z. Anorg. Allgem. Chem.* **279**:28 (1955)
b. Glemser, O., and Schröder, H., *Z. Anorg. Allgem. Chem.* **284**:97 (1956)
c. Glemser, O., and Haeseler, H., *Z. Anorg. Allgem. Chem.* **287**:54 (1956)
d. Schröder, H., and Glemser, O., *Z. Anorg. Allgem. Chem.* **298**:78 (1959)
e. Rickert, H., and Glemser, O., *Z. Anorg. Allgem. Chem.* **307**:328 (1961)
13. Logothetis, A.L., Sausen, G.N., and Shozda, R.J., *Inorg. Chem.* **2**:173-175 (1963)
14. Baddour, R.F., and Blanchet, J.L., *Ind. Eng. Chem. Process Design Develop.* **3**:258 (1964)
15. Baddour, R.F., and Bronfin, B.R., *Ind. Eng. Chem. Process Design Develop.* **4**:162-166 (1965)
16. Freeman, M.P., "The Nature and Quantitative Determination of the Reactive Species in a Nitrogen Plasma Jet," presented to the 147th National Meeting of American Chemical Society, April 5-10, 1964, Philadelphia, Pa.
17. Lipscomb, R.D., and Smith, W.C., U.S. Patent 3,008,798, Nov. 14, 1961
18. John, R.R., and Bade, W.L., *ARS J.* **31**:4-17 (1961)
19. Skifstad, J.G., "Summary of Published Literature Concerned with Electric Arc Phenomena Pertinent to Plasma Jet Devices," Technical Report No. TM-62-4, Jet Propulsion Center, Purdue University, Aug. 1962
20. "No. F-40 Plasma Torch," Thermal Dynamics Corp., Lebanon, N.H.
21. Freeman, M.P., and Skrivan, J.F., *A. I. Ch. E. J.* **8**:450-454 (1962)
22. Plooster, M.N., and Reed, T.B., *J. Chem. Phys.* **31**:66-72 (1959)
23. Timmins, R.S., and Ammann, P.R., "Chemical Reactions in a Constricted Arc," presented to the 57th Annual Meeting, American Institute of Chemical Engineering, Dec. 7, 1964, Boston, Mass.
24. Jahn, R.E., *Brit. J. Appl. Phys.* **14**:585-588 (1963)
25. Hilsenrath, J., and Klein, M., "Tables of Thermodynamic Properties of Nitrogen in Chemical Equilibrium, Including Second Virial Corrections, From 2000 to 15,000°K," Tech. Doc. Rept. No. AEDC-TDR-63-162, Arnold Engineering Development Center, Mar. 1964
26. Busz, G., and Finkelnburg, W., *Z. Physik* **139**:218 (1954)
27. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, Jan. 1961
28. Cruise, D.R. *J. Phys. Chem.* **68**:3797-3802 (1964)
29. White, W.B., Johnson, S.M., and Dantzig, G.B., *J. Chem. Phys.* **28**:751-755 (1958)
30. Heicklen, J., and Knight, V., *J. Phys. Chem.* **69**:2484 (1965)
31. Middleton, W.J., U.S. Patent 2,831,835, Apr. 1958
32. Stokes, C.S., Knipe, W.W., and Steng, L.A., *J. Electrochem. Soc.* **107**:35-38 (1960)
33. Grey, J., Jacobs, P.F., *AIAA J.* **2**:433-438 (1964)
34. Fawcett, F.S., and Lipscomb, R.D., *J. Am. Chem. Soc.* **82**:1509-1510 (1960)
35. Haszeldine, R.N., *Chem. Soc. (London) Annual Rept. on Prog. Chem.* **51**:281 (1954)
36. Colburn, C.B., Johnson, F.A., Kennedy, A., McCallum, K., Metzger, L.C., and Parker, C.O., *J. Am. Chem. Soc.* **81**:6397-6398 (1959)
37. Maya, W., *Inorg. Chem.* **3**:1063 (1964)

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE SYNTHESIS OF NITROGEN FLUORIDES IN A NITROGEN PLASMA JET			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) A final report on one phase of the problem.			
5. AUTHOR(S) (Last name, first name, initial) Bronfin, B.R., and Hazlett, R.N.			
6. REPORT DATE January 12, 1966		7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 37
8a. CONTRACT OR GRANT NO. NRL Problem C01-05		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6340	
b. PROJECT NO. RR 010-01-44-5851		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research)	
13. ABSTRACT <p>Nitrogen-fluorine compounds have a high energy content, which makes them of interest in the propellant field. An electric arc technique, which has been used in the synthesis of other high-energy compounds, has now been applied to the nitrogen-fluorine system. A nitrogen plasma jet was intermixed with gaseous fluorides (CF_4 or SF_6) and subsequently quenched. Small yields of NF_3, N_2F_4, and CF_3NF_2 were produced, together with trace quantities of other products.</p> <p>The observed products have been accounted for by a reaction sequence involving the formation of FCN and its subsequent stepwise fluorination by addition at the triple bond. FCN is only an intermediate, however, and has not been found in the product stream.</p> <p>The yield of fixed-nitrogen products is about 1% of inlet nitrogen for typical conditions, and it increases with increasing power input and increasing F/N ratio in the plasma.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nitrogen fluorides High-energy compounds Rocket propellants Nitrogen plasma Plasma jet Quenching Fluorination Synthesis by plasma jet						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.