

HYDROCARBON-NITROGEN REACTIONS IN A THERMAL INDUCTION PLASMA

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Gas temperatures above 15,000 K have been observed in plasma generated by radio-frequency induction coupling¹. This high thermal energy regime becomes of interest to the chemist for the investigation of highly endothermic reactions. In particular, this paper will report reactions between methane and nitrogen fed to a thermal induction plasma and subsequently quenched to yield hydrogen cyanide, acetylene and hydrogen.

PREVIOUS STUDIES OF THE H-C-N SYSTEM

Low Pressure Discharges. Winkler and his co-workers²⁻⁵ have systematically studied the reactions of nitrogen, activated by passage through a high-voltage discharge, with various hydrocarbons. These studies were carried out at pressures near 1 torr with very low reagent flow rates. Gas temperatures were also low, typically 300 C. In this nonequilibrium system the reaction between methane and "active" nitrogen yielded hydrogen cyanide, acetylene and hydrogen².

High Pressure Arcs. More recently high-power thermal arcs were used for the study of the H-C-N system near atmospheric pressure. Leutner⁶ operated a nitrogen plasma jet into which methane was mixed. In his briefly reported results, up to 10 percent conversion of the nitrogen to HCN was found. At this symposium Freeman⁷ has reported an extensive study of the synthesis of HCN from a nitrogen plasma jet intermixed with methane. Typically, a 7 percent conversion of N₂ to HCN was observed. In both studies H₂, C₂H₂, and unreacted CH₄ were also identified as major constituents in the cooled product stream.

If the maximum mean temperature attainable in these previous studies is calculated, one finds that enthalpy input was insufficient to generate mean temperatures greater than ~ 5000 K.

Dissociating Plasmas. Upon considering the various species possible in the H-C-N system, the strongest bond found is N≡N (226 kcal/g-mole). Thermal dissociation of N₂ is essentially complete at temperatures in excess of 8000 K⁸. One can envision a high-pressure, stable plasma fed with any of a variety of carbon, hydrogen, or nitrogen compounds and supplied with sufficient enthalpy to reach this high temperature range. The constituent species of such a plasma would be primarily atomic nitrogen, atomic hydrogen, and atomic carbon near 10¹⁷ cm⁻³ concentration. The result of rapidly quenching such a highly reactive atom mixture has been generally unexplored. Ammann and Timmins^{9,10}, however, did study the rapid quenching of the simpler atomic-nitrogen/atomic-oxygen mixtures at 10,000 K

and 1 atm, which were generated by a constricted d.c. arc. The study which is reported in this paper was undertaken to explore the chemical composition of mixtures formed by the rapid quench of atomic-nitrogen/atomic-carbon/atomic-hydrogen mixtures.

PLASMA REACTOR

Radio-frequency Induction Plasma. One convenient approach to achieve the required temperatures in excess of 10,000 K at atmospheric pressure is generation of a thermal plasma by radio-frequency induction heating. The techniques for generating and containing a stable high-temperature induction plasma have been described in detail by Reed^{1,11}, Mironer¹², Marynowski and Monroe¹³, Freeman and Chase¹⁴, and Thorpe¹⁵. Figure 1 presents a diagram of the plasma generator used. A few turns of copper tubing were wound around the outside of a water-cooled quartz reactor tube. This coil inductively coupled the supplied r.f. power into the gaseous reactants sent through the reactor. A water-cooled sampling tube with very small internal diameter which served to quench rapidly the reactive plasma species is shown. Efficient cooling allowed the entrance tip of the quench tube to be placed directly into the plasma core.

A cross-sectional diagram of the reactor is presented in Fig. 2. The isotherms indicated are those determined spectroscopically by Reed¹ and are representative of conditions in this study. No direct temperature measurements were attempted in the present study.

The Induction Plasma as a Chemical Reactor. Several characteristics of this system can be exploited for chemical synthesis:

1. Average temperatures in excess of 10,000 K allow essentially complete molecular dissociation. (Lower power input can reduce the specific enthalpy to preserve desired free radicals.)
2. Plasma stability is maintained while operating at very low gas velocities (<1 cm/sec). Thus long residence times and efficient mixing are achieved.
3. The power coupling involves no contact of electrodes with the plasma. Therefore electrode corrosion and contamination are eliminated, and with sufficient input power, thermal plasmas of any stoichiometry can be stabilized.
4. Quenching rates on the order of 10^7 K/sec can be achieved in the sampling probe. Thus the high heat of reaction released as the plasma species recombine is efficiently absorbed.

The system actually is comprised of two reactors in series: I. the plasma reactor, wherein high-temperature transient species are generated, followed by II. the quench reactor, wherein the plasma precursors are rapidly cooled within the cold-walled sampling tube to yield room-temperature stable products.

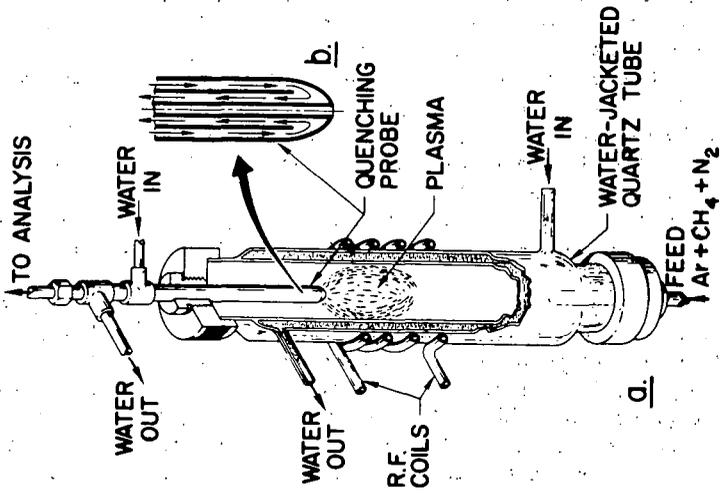


Figure 1 (a) Diagram of radio-frequency induction plasma reactor.
 (b) Cross-section of water-cooled quenching probe.

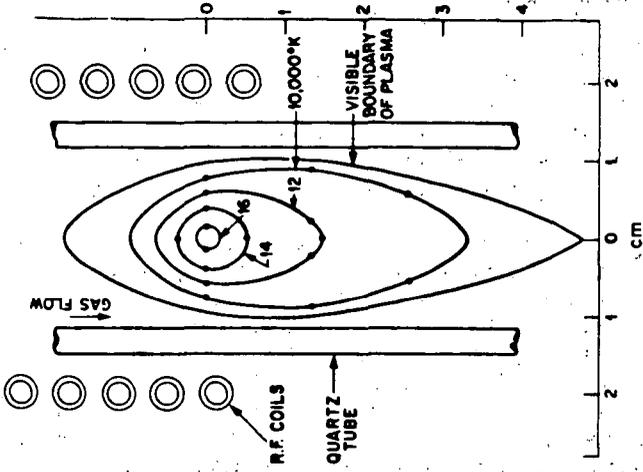


Figure 2 Isotherms in pure argon at 1 atm (1).

PLASMA COMPOSITION

Thermochemical Equilibrium. One of the unique features of the thermal induction plasma is stable operation with low gas flow. Since flow velocities in the plasma zone are typically a few centimeters per second, residence times on the order of a second are associated with plasma species. In a plasma near atmospheric pressure the particle mean free path is very short and the collision rate very high. At plasma temperatures (c. 10,000 K) gas phase reactions can be expected to proceed quite rapidly. These facts lead to the initial assumption that local plasma composition approaches thermodynamic equilibrium.

The H-C-N System. The theoretical compositions of hydrogen-carbon-nitrogen mixtures at thermodynamic equilibrium have been computed by Kroepelin, et al.¹⁶, Marynowski, et al.¹⁷, and Bronfin, et al.¹⁸, for a variety of conditions. Computations were based on free energy minimization using tabulated thermochemical data¹⁹. Figure 3 presents calculated equilibrium composition data for a typical stoichiometry: H:C:N = 4:1:2, ($\text{CH}_4/\text{N}_2 = 1$), at 1/2 atm (380 torr). Only species whose concentration is greater than 1.0 mole-percent are shown on this plot; however, twenty-one different chemical species were considered. In Fig. 3a, full equilibrium was considered for a two-phase system which included graphite. Figure 3b shows that temperature segment which is altered by the exclusion of the solid-phase, C(s).

Molecular nitrogen, N_2 , is a major constituent over a broad range up to 8000 K; thereafter thermal dissociation results in the predominance of atomic nitrogen, N. As mentioned above, at temperatures over 8000 K, not shown of the graph, the system becomes completely dissociated into a simple three-component atomic state: H, C, N. At temperatures greater than 7000 K significant thermal ionization occurs, generating significant concentrations of singly-ionized atoms, e.g., C^+ , H^+ , N^+ . As noted in both plots, CH_4 dissociation is well underway at 1000 K, resulting in the formation of H_2 and C(s) in the two-phase system (a); but the formation of HCN and C_2H_2 in the single-phase system (b). At temperatures above 3000 K, C_2H_2 begins to fragment to C_2H and H, and with increasing temperature, to the atomic species. At temperatures above 3800 K, HCN begins to fragment to CN and H, and with increasing temperature, to the atomic species. Nitrogen-hydrogen species, e.g., NH_2 , occur at concentrations below 0.01 mole-percent over the entire range plotted.

In comparing the common temperature segments of the single-phase and two-phase composition diagrams, important differences are noted in that: (1) higher concentrations of species like HCN and C_2H_2 are preserved at lower temperatures in the single-phase case, and (2) the maximum concentration of these species is somewhat higher in the single-phase case. Hence in the lower temperature range, the predicted yield of HCN and C_2H_2 is enhanced by retarding carbon nucleation. This kinetic limitation acts to freeze the mixture composition at around 2700 K so that negligible composition change is predicted over a fairly broad temperature interval, down to 1500 K.

Composition of the Plasma. No direct determination of the plasma composition was attempted in the present study. Only a few efforts in this direction have

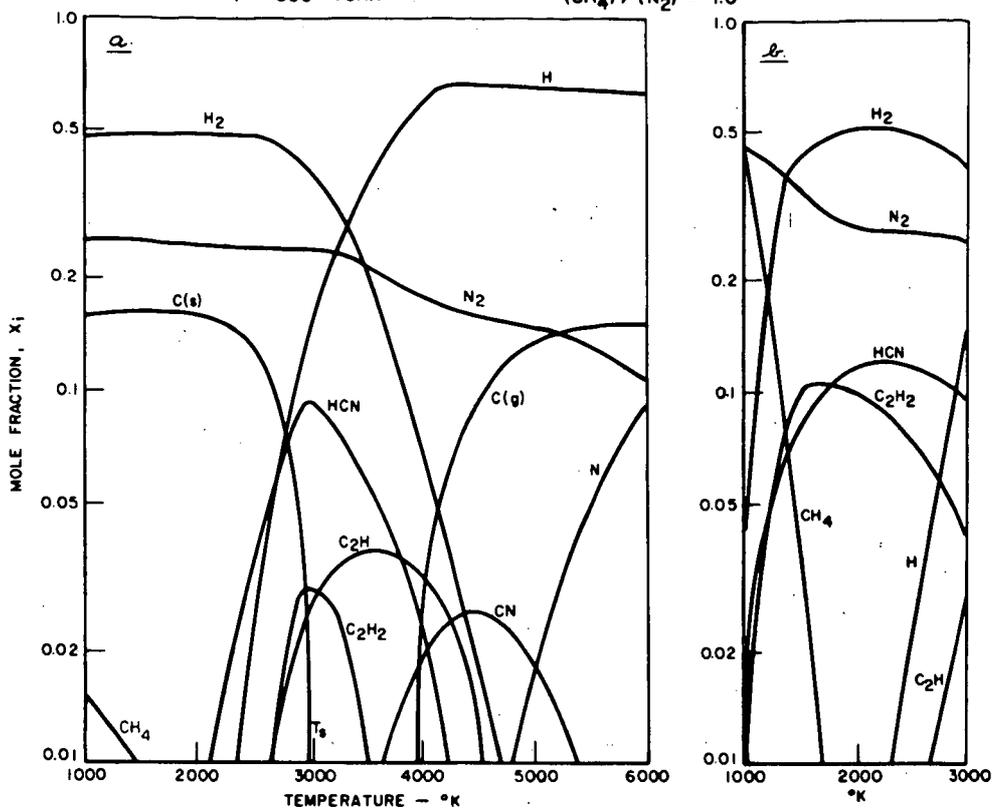


Figure 3 Equilibrium composition of equimolar CH₄-N₂ mixture. (a) Including solid carbon; (b) Excluding solid carbon. Region above T_s common.

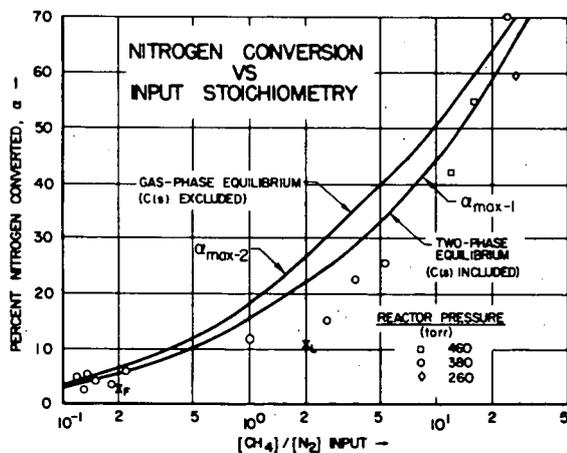


Figure 4 Yield of HCN, expressed as percent N₂ converted, as a function of input stoichiometry. Solid lines show maximum yield predicted by thermodynamic equilibrium. Data points show experimental results from the plasma reactor: Ar flow rate 42 std cc/sec, total reagent flow rate 2 std cc/sec, net power ~ 3.5 kw. Reactor pressure identified with key. Points labeled x from plasma jet studies^{6,7}.

appeared in the literature. O'Halloran, et al.²⁰, have directly sampled an argon plasma jet using a specially designed entrance cone opening to a time-of-flight mass spectrometer. Raisen, et al.²¹, have made spectroscopic identifications of species in an air plasma. Unlike the mass spectrometer measurements, however, emission spectroscopy is difficult to quantify due to the wide variance in the oscillator-strengths of the likely emitters.

Faced with the difficulty of determining plasma composition directly, one is prone to apply equilibrium predictions as a guide to local plasma composition. Referring both to Figs. 2 and 3, a highly dissociated composition can be expected in most of the plasma region. Temperatures in excess of 10,000 K, expected over most of the central region of the plasma, would dictate that the atomic species H, C, and N, and their ions would predominate.

QUENCHING

At this juncture it is important to ask what changes in composition would be encountered on cooling the H-C-N atom plasma. A slow, gradual cooling of the labile intermediates resident in the plasma zone may well allow the system to revert to the original reactants along an equilibrium path. Kroepelin and Kipping²² found this effect in their study of a 10 amp, 40 volt d.c. arc burning in a hydrocarbon-nitrogen atmosphere. The composition of the slowly cooled arc-heated gases was found to be mainly N₂, H₂, and C₁ and C₂ hydrocarbons. No HCN was observed. Under extremely rapid cooling, however, kinetic limitations can interpose along the reaction path to yield different, more interesting or valuable products.

The Cold-Wall Tube. A small-diameter, water-cooled tube was selected from the variety of available high-cooling-rate devices, to provide rapid and convenient quenching of the plasma species. Figure 1b shows a diagram of the simple design of the three-concentric tube arrangement of the quenching probe²³. The overall outside diameter of the probe was 3/8 in. The internal diameter of the quenching tube which receives the hot plasma was 0.032 in. The surfaces of the inner tube were stainless steel; other parts were fabricated from copper. The effect of a variation in the composition of the cold surface was not studied.

Cooling Rate. Due to the high rate of heat transfer from plasma to adjacent cold wall, rapid cooling occurs in the quenching tube. Freeman and Skrivan^{24,25} have measured an initial temperature decay rate of 5×10^7 K/sec in water-cooled tubes. In their model of the heat-transfer process occurring in very small tubes, Ammann and Timmins¹⁰ have calculated cooling rates greater than 10^9 K/sec. Probably quenching rates in this range were associated with the quenching tube used in this study.

Reaction Path During Quench. Unfortunately, there is a sparsity of high-temperature kinetic data for the H-C-N system. Hence one is unable to predict with certainty the reaction path followed as the atomic species H, C, and N, are cooled from 15,000 K to 500 K in 10 milliseconds, for example. After an examination of

the experimental results in the succeeding sections, it may be possible to infer the important steps in the reaction sequence.

EXPERIMENTAL CONDITIONS

Radio-frequency Supply. A commercially available²⁶ 12 kw (nominal) induction heater, oscillating at 4 MHz, was the power source for the experiment. The load coil, shown in Fig. 1, consisted of five turns of 1/4-in. o.d., water-cooled, copper tubing wound tightly around the quartz reaction tube. The overall height of the coil was 1 1/2 in., with a central diameter of 3 in.

Reactor. Containment of the plasma was accomplished within a 35 cm long, 47 mm i.d. quartz tube, mounted vertically. The high-power loadings necessitated cooling which was afforded by flowing 1/3 gpm of water into a cooling jacket surrounding the central reaction tube. The plasma-forming gases were premixed and sent into the tube through a brass fitting sealed onto the tube base. Gas flow rates were monitored with calibrated rotameters. Plasma-heated gases left the reaction tube through a second brass fitting sealed onto the top of the tube. This cap, which was of approximately 1 liter volume, was water-cooled. In this configuration the top fitting functioned as a cooling chamber to reduce the average gas temperature to within a few degrees of ambient. The system pressure was controlled by a high-capacity regulated vacuum line attached to the upper cap.

A sliding O-ring seal was provided at the center of the upper cap for positioning of the 3/8-in. o.d. by 0.032-in. i.d. quench probe along the central axis of the reaction tube. Cooling water was supplied to the quench probe at a metered rate of 1/3 gpm. The entrance tip of the probe was typically located at the center of the uppermost winding of the load coil.

The flow rate through each cooling water line was metered with calibrated rotameters which were placed downstream of liquid pressure regulators. Inter-consistent mercury thermometers were mounted at each cooling water line inlet and outlet. By measurement of the temperature rise and flow rate in each cooling line, total enthalpy delivery rates could be determined.

Chemical Analysis. The gas stream withdrawn through the quench probe was sent to an on-line gas chromatograph for quantitative analysis. A triacetin column, recommended by Isbell²⁷, followed by a molecular sieve column, recommended by Purnell²⁸, was used for resolution of chromatogram peaks. This configuration allowed the detection of the following compounds with a thermal conductivity cell: HCN, H₂, Ar, N₂, CH₄, and various higher hydrocarbons. A parallel flame-ionization detector was useful for detecting low concentrations of hydrocarbons, e.g., CH₄, C₂H₂.

Experimental Variables. Total pressure in the plasma reactor was typically 380 torr; some data were also acquired in a range from 160 to 760 torr. For the data reported here the argon feed rate was 42 std cm³/sec (6.5 g-mole/hr). This

flow rate insured good plasma stability for the available r.f. power and remained with the capacity of the subatmospheric pressure regulating equipment. Added reagent gases were fed at 1/50th to 1/10th that rate, with the molal ratio varied over a broad range: $0.1 \leq \text{CH}_4/\text{N}_2 \leq 25$. The power coupled into the gas mixtures was ~ 3.5 kw maximum, as determined from the summation of cooling water heating rates.

In the later stages of the experiment various nitrogen-substituted hydrocarbon liquids were fed to the argon plasma, namely: CH_3CN , $\text{CH}_3\text{CH}_2\text{CN}$, and CH_2CHCN . Special modifications to the gas-flow system were made to insure injection of these nitriles into the plasma. A part of the argon feed stream was split off to a sealed gas-liquid bubbler containing warmed reagent. Since these compounds are all relatively volatile, a substantial amount of nitrile entrainment occurred. Rather than introduce the nitrile-laden argon stream into the relatively cool gas region at the base of the reaction tube, a special injection probe was provided to introduce the stream into the hot plasma region. This second water-cooled probe was positioned through an O-ring seal in the base cap. The probe design was identical to that previously described for quenching (cf. Fig. 1b). The tip of the injector probe was placed at the center of the lowermost winding of the load coil. Material exiting the injector thus was assured of entering the plasma zone.

EXPERIMENTAL RESULTS

Plasma Stability. Over the entire range of experimental variables the plasma was stable and brightly luminous. The luminous region of the plasma appeared to fill about 90 percent of the cross-sectional area of the cooled quartz tube and extended from the bottom to about 3 in. above the r.f. load coil. With high hydrocarbon flow rates a gradual build-up of soot occurred on the quartz tube walls.

Methane-Nitrogen Reactions

Products of Reaction. A quantitative analysis of the gas stream withdrawn through the quenching probe was made for each run. Over the entire range of stoichiometric studies, the methane fed to the plasma was completely reacted; no methane was detected in the quenched gas stream. The following major reaction products were identified: HCN , C_2H_2 , H_2 . Also present were Ar and unreacted N_2 .

Nitrogen Conversion. Since essentially complete conversion of methane was observed for each run, the varying conversion of nitrogen was selected as an important datum. If the mole fraction of a species i found in the quenched product stream is defined as x_i , then the conversion of nitrogen, defined as α is given by:

$$\alpha = \frac{\frac{1}{2} x_{\text{HCN}}}{x_{\text{N}_2} + \frac{1}{2} x_{\text{HCN}}}$$

Figure 4 shows the percent conversion of nitrogen as a function of feed stoichiometry, CH_4/N_2 . The argon feed rate for these runs was fixed at 42 std cm^3/sec . The total flow rate of the reactant mixture was typically 2 std cm^3/sec . The key at the bottom right of the figure identifies the reactor pressure for each data point.

The measured conversion of nitrogen varied from 3 percent at the lowest stoichiometry considered, $\text{CH}_4/\text{N}_2 = 0.1$, to a maximum of 70 percent at a methane-rich stoichiometry, $\text{CH}_4/\text{N}_2 = 2.5$. This high value of nitrogen fixation is considerably in excess of previously reported nitrogen conversion levels observed in thermal plasma reactions. Pressure variations had no significant effect.

Typical Product Composition. Table I, below, presents the composition of the product stream produced under typical conditions.

Table I

Typical Product Composition

Reactor Pressure - 380 torr		Net Power Input - 3.5 kw	
<u>Input</u>	<u>Feed Rate</u> (std cc/sec)	<u>Feed Composition</u> (mole-percent)	
Ar	41.8	97.6	
N_2	0.5	1.2	
CH_4	0.5	1.2	
Total	42.8	100.0	
<u>Product</u>	<u>Composition</u> (mole-percent)	<u>Composition</u> (mole-percent, Ar-free)	
Ar	96.5	-	
H_2	2.0 ^a	57	
N_2	1.0	29	
HCN	0.3	9	
C_2H_2	0.2	5	
CH_4	trace	-	
Total	100.0	100	

Note a: Compositions determined from gas chromatograms; \pm 10 percent.

As was seen in Fig. 4, Table I shows that about 12 percent of the nitrogen fed at this stoichiometry was converted to hydrogen cyanide. Ninety-nine percent of the methane fed was converted to the gaseous products hydrogen and acetylene and also

to an unmeasured small quantity of solid product which deposited on the wall. The minor disparity between the nitrogen and carbon material balances indicates the small fraction of material lost from the reaction zone to deposition on the reactor walls.

Nitrile Reactions

Products of Reaction. Small quantities of nitriles could be continuously fed to the argon plasma by using the modified injection arrangement (described in the previous section). Mixed plasma which was quenched by withdrawal through the water-cooled probe was analyzed with no change in the gas chromatograph. Essentially complete conversion of the lower molecular weight compounds, acetonitrile, CH_3CN , and acrylonitrile, CH_2CHCN , was observed. A minor amount (~10 percent) of propionitrile, $\text{CH}_3\text{CH}_2\text{CN}$, was observed in the quenched gas stream, perhaps due to a bypassing of the plasma core. Each of the nitriles produced the same reaction products, a repeat of those produced in the methane-nitrogen study. High concentrations of HCN , C_2H_2 , H_2 , and N_2 were observed along with the argon diluent. A complete quantitative chemical analysis of these nitrile runs has not, as yet, been performed.

DISCUSSION OF RESULTS

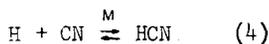
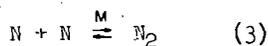
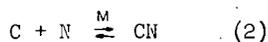
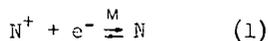
Variance in the Conversion Percentage. Considerable variance in the fraction of nitrogen converted was observed among repetitions of runs with constant stoichiometry, net power input, and pressure. The data points plotted in Fig. 4 include the maximum observed conversion levels for each stoichiometry. Sources of error in the experimental procedure which could have scattered the data down from maximum conversion were:

1. Improper adjustment of r.f. supply controls so as to mismatch the supply and plasma impedance, perhaps generating plasma irregularities
2. Minor air leaks which would add additional nitrogen to the plasma to alter the stoichiometry from preset values
3. Deposition of carbon or hydrocarbon material on the reactor walls or, the reverse, significant vaporization of carbon from the walls, to alter the preset stoichiometry.

Thermochemical Equilibrium Predictions. As described in the "Plasma Composition" section, above, a full range of composition calculations were made assuming thermochemical equilibrium. These calculations predicted that the plasma composition within the r.f. coil would be dominated by atomic species for the specific power input used in this study. Perhaps the following additional consideration of these theoretical predictions can elucidate the processes occurring during rapid quench.

Freezing. Hypothesize that equilibrium is followed during the initial stages of cooling within the quench tube. For heuristic purposes, assume that equilibrium is obeyed during temperature decay to approximately 3000 K, or more specifically, to that temperature where equilibrium predicts the maximum number of moles of HCN to be formed. Then assume that all reactions involving nitrogen species are frozen at that point, so that even as cooling continues negligible decomposition of the HCN occurs.

Chemical Reaction Kinetics. In making this series of seemingly unwarranted assumptions, some specific reaction rates have been implied to be very fast, while others, very slow. Focusing on nitrogen-containing species, the following types of reaction have been assumed to be rapid under the conditions developed in the quenching tube:



Further, the following have been assumed to be very slow:



To date a full description of the reaction kinetics of the H-C-N system, even at moderate temperatures, is unavailable. In the recent shock tube study of Marshall, Jeffers, and Bauer²⁹, preliminary results indicate that the equilibrium in Reaction 4 may be achieved rapidly at elevated temperatures. However, the evidence points to a rather complex reaction mechanism for the thermal dissociation of HCN, wherein many more steps are involved than mentioned here. The complexity of this system was encountered in the earlier study of Robertson and Pease³⁰, and in similar systems explored by Goy, Shaw and Pritchard³¹.

Rapid dissociation/recombination rates have been determined for nitrogen, Reaction 3, by Wray³². Reaction rate data is not available for Reaction 2, nor for other reactions likely to be quite important in the H-C-N system.

Atomic-ion/electron recombination reactions for each of the three atoms in the plasma are likely to be rapid³³ relative to the quenching time.

In summary, existing reaction rate data is far from sufficient to check the assumptions made about the reaction mechanisms appropriate to this H-C-N system. Additional kinetic studies which generate presently unknown reaction rates are needed before an accurate reaction path can be predicted theoretically for the reacting H-C-N system.

Composition at the Assumed Freezing Point. The validity of this freezing approach can be found comparing the predicted composition at the freezing temperature with the observed composition of the quenched gas stream. The following variables are defined for Table II, which facilitates the comparison.

For the equilibrium calculations let the input stoichiometry be characterized by the molar ratio $[\text{CH}_4]/[\text{N}_2]$, set equal to ϕ ; let n_{N_2} be the number of moles of N_2 introduced; and let n_i^* be the number of moles of species i present at equilibrium at a pressure, P , and a temperature, T . Then T_f is established for a given ϕ and P , as the temperature at which equilibrium predicts the quantity $n_{\text{HCN}}^*/n_{\text{N}_2}$ is a maximum.

Table II shows the mole fraction of the predominant species for a T_f value found in an equimolar input stoichiometry. As mentioned in the "Plasma Composition" section, above, solid-carbon formation may be retarded in this system. Therefore, a second set of mole fraction data have been presented in Table II which excludes the species $\text{C}(s)$ from the calculation.

Table II

Calculated Equilibrium Composition at the Temperature
where HCN Yield is Maximized

Pressure - 380 torr		$\phi \equiv [\text{CH}_4]/[\text{N}_2] = 1.0$		
Mole Fractions				
	Including $\text{C}(s)$ $T_f = 3050 \text{ K}$		Excluding $\text{C}(s)$ $T_f = 2500 \text{ K}$	
	x_i	x_i^a	x_i	x_i^a
H_2	0.421	0.543	0.497	0.522
N_2	0.252	0.283	0.266	0.274
HCN	0.097	0.109	0.120	0.124
C_2H_2	0.038	0.065	0.073	0.080
H	0.144	-	0.025	-
C_2H	0.020	-	0.005	-
others	0.030	-	0.014	-
	$\frac{n_{\text{HCN}}^*}{n_{\text{N}_2}} = \alpha_{\text{max}-1} = 0.161$		$\alpha_{\text{max}-2} = 0.185$	

Note a: Adjusted to allow for the reactions: $\text{C}_2\text{H} + \text{H} \rightarrow \text{C}_2\text{H}_2$, $2\text{H} \rightarrow \text{H}_2$.

Frozen Composition Calculation versus Experimentally Observed Composition.

If, indeed, the original assumption that important reactions occurring in the gas withdrawn from the plasma into the cold quenching tube are frozen in the vicinity of 3000 K is valid, then agreement should be found between the compositions listed in Tables I and II. In comparing the argon-free composition listed in Table I with Column 2 in Table II, relatively good agreement is found.

This comparison has been extended to the full range of stoichiometries studied. On Fig. 4, the maximum nitrogen conversion, $\alpha_{\max-1}$, and $\alpha_{\max-2}$, has been plotted against input CH_4/N_2 -mole ratio, ϕ . The subscript 1 refers to calculations including C(s); subscript 2, to excluding C(s). Agreement between the freezing model and observed results is very good over more than a two-decade range in stoichiometry variation. These results strongly support the freezing model in the overall reaction path. With the existing scatter of the data, a delineation between the single-phase and two-phase equilibrium predictions of composition at T_f is not possible. Additional experimental runs may lessen this ambiguity. The retardation of carbon solid formation, however, accounts for less than a 10 percent change in predicted maximum nitrogen conversion, on the average.

Freezing Temperature. The data do not allow an exact determination of a freezing temperature appropriate to the quenching process. Referring back to Fig. 3a, a change of a few hundred degrees in the assumed T_f could account for the data points which indicate 10 to 20 percent less than the two-phase equilibrium predictions of maximum nitrogen conversion. Fig. 3b shows the HCN concentration plateaus to be quite broad. Hence the nitrogen conversion prediction would be relatively insensitive to variation in freezing temperature over the range from 1500 to 3000 K. Future experimental refinements may allow a more exact determination of T_f .

Observed Compositions in Nitrile Experiments. An analysis of the maximum nitrogen conversion predicted by thermochemical equilibrium has not been made for the different nitrile inputs described in the "Experimental Conditions" section. The similarity of product distribution and of the ratio of HCN to N_2 in the product points to the same reaction mechanisms as in the CH_4/N_2 studies.

Correlation with Studies by Other Investigators

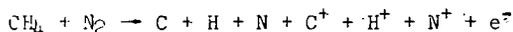
If the proposed reaction mechanism is correct, then the yields found in other studies of the synthesis of HCN by thermal reactions of hydrocarbons with nitrogen should not exceed the predicted values of α . Some results of the production of HCN in plasma jets have been reported, as was mentioned in the "Previous Studies" section. While the differences in design between the plasma jet and induction plasma reactors are not detailed here, sample results from these other studies are plotted on Fig. 4. The maximum nitrogen conversion values observed in the nitrogen plasma jet experiments of Leutner¹¹ (designated α_L) and Freeman¹² (designated α_F) appear. These experimental data points are seen to lie below the maximum nitrogen conversion prediction.

The phenomena in the plasma jet experiments which convert less nitrogen than the maximum predicted by the freezing model may well be linked to a mixing or diffusion rate (CH_4 and N_2 were not premixed) or to temperatures insufficient to reach T_f . This question is the subject of a separate theoretical analysis now in progress by the author.

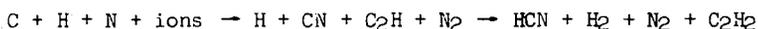
THE REACTION SEQUENCE

The experimental data support the following description of the overall reaction sequence:

1. Plasma Reactions. Feed reagents are dissociated to their atomic constituents in a thermal plasma. Some thermal ionization occurs at sufficiently high temperatures.



2. Initial Cooling. Plasma taken into a small-diameter cold tube rapidly cools with chemical reactions following equilibrium.



3. Frozen Reaction Kinetics. Rapid cooling continues, but at a rate much greater than the progress of the apparently complex reaction sequence necessary to destroy the species HCN , C_2H_2 , and H_2 . Hence the composition of the cooling gas is frozen at the end of Step 2.

Evidence for the Freezing Model in Other Reacting Systems. The freezing model likely is applicable to a wide variety of reacting thermal plasma systems which employ a rapid quench. Ammann and Timmins¹⁵ found a mechanism involving the freezing of equilibrating reactions to be applicable to their study of the quenching of nitrogen-oxygen plasma. Aided by a wealth of published rate data on chemical reactions in air, they were able to model the time-temperature-composition history of N-O plasma cooling within small-diameter tubes. A quite similar freezing temperature, T_f , was found at 3500°K for that system. The equilibrium composition of nitric oxide, NO , at T_f was preserved during continued rapid cooling.

CONCLUSIONS

Mixtures of methane and nitrogen can be fed continuously to a thermal argon induction plasma maintained above 10,000 K. A rapid quench of the heated plasma mixture produces HCN , C_2H_2 , and H_2 . Final yields of HCN , expressed as a fraction of the nitrogen converted, range between 3 and 70 percent, a function of the input stoichiometry.

The reaction proceeds by the complete dissociation of the feed reactants in the plasma to yield a mixture of H, C, and N. As this mixture is quenched, the reaction initially proceeds along an equilibrium path, forming HCN, C₂H₂, H₂, and N₂. Below the temperature where the equilibrium yield of HCN is maximized, the slower rearrangement reactions and carbon nucleation are frozen by the rapid cooling, so that negligible alteration in the gas composition occurs upon further cooling.

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