Gas Composition Measurements in Arc Heated Flowfields via Mass Spectrometry

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Gas compositions for an arc heated flowfield were determined by mass spectrometry on gas samples drawn from the flowfield through a sample probe. Surveys were made across the freestream flow using sample probes made of copper and quartz. Oxygen atoms reaching the mass spectrometer ranged from 6 to 9.4% and was a direct function of arc heater current and resultant stream enthalpy. Likewise, mole percents of nitrogen atoms ranged from 13.5 to 19 for total enthalpies of 7.0 to 18.4 MJ/kg. Species gradients existed in both the radial and axial directions. Atomic concentrations were highest near the centerline and at the nozzle exit. Some skewness off the centerline in the concentration profiles was noted. A species survey was completed around a shock that was established by a copper blunt body placed in the flowfield. The results showed strong species gradients following the shock edge, with atom mole fractions highest along the shock edge. Overall, the results provide insight into gas composition by point measurements in arc heated flowfields. The results suggest that nitrogen may begin dissociating before all of the oxygen dissociates and that past assumptions based on frozen chemistry models may be faulty.

Nomenclature

C_i = atom concentration for species i, kg mole/m^3
c = mean velocity of the reacting species, m/s
D = diffusion coefficient, m^2/s
Dp = diffusion-pressure constant, m^2 Pa/s
Ea = activation energy, kJ/atom
K = dimensionless rate constant for homogeneous recombination reaction
k = Boltzmann constant, kJ/atom K
k_i = rate constant for the homogeneous recombination reactions
L = length of the sample probe, m
M = concentration of third bodies, kg mole/m^3
m/e = mass to charge ratio relative to $H^+ = 1$
n = atom concentration at any z distance along the sample probe, atoms/m^3
P = pressure, mbar or Pa
Q = volumetric gas flow rate, m^3/s
R = radius of the tube, m
R_g = gas constant, 8314 J/(kg mole K)
r = rate of atom recombination, kg mole/s m^3 or radial position in a tube, m, or probe radial position in vacuum chamber, m
T = temperature, K
v = velocity in the tube, m/s
X_i = mole fraction of species i
α = ith root of the equation $J_0(\alpha_i) = \alpha\delta J_1(\alpha_i)$
β = dimensionless quantity dependent on root mean square of dimensionless velocity, dimensionless rate constant, and alpha
δ = dimensionless quantity related to the wall recombination coefficient, defined in Eq. (4)
γ = probe wall recombination coefficient, fraction of atoms which recombine after striking a wall
λ = dimensionless probe length, L/R
ν = dimensionless velocity, $(vR)/(2D)$

Subscripts

L = length of tube
0 = conditions related to the inlet of the tube

Introduction

KNOWLEDGE of atomic and molecular concentrations in boundary and shock layers is of great importance in the design of thermal protection systems (TPS) for re-entry systems, particularly the way atom concentrations relate to catalytic recombination on thermal protection surfaces. Despite this requirement, only indirect determination of concentration fields is available based on computational fluid dynamics using nonequilibrium reacting chemistry. These calculations must then be related to actual heating rates observed in re-entry and ground test environments in order to match the observed heating rates. If actual atomic and molecular species concentrations could be determined for various flight and ground test conditions, a large set of estimated quantities (species concentrations) could be better predicted. Thus, if direct determination of species concentrations could be performed in a re-entry simulation environment like the NASA Johnson Space Center (NASA-JSC) Atmospheric Reentry Materials and Structures Evaluation Facility (ARMSEF), better information would be available to use in TPS design models.

The purpose of this work was to evaluate direct sampling via a mass spectrometer in which sample residence time was less than 1 s. Further, preliminary work included the evaluation of atom recombination in various sample probe environments.

Long term benefits of this project will be the introduction of proper species concentrations into shock and surface chemistry models used in TPS design.

Background

Quadrupole ionization mass spectrometry is a well-developed technique used for the determination of gas compositions via mass separation.[1] There are two major obstacles to successful mass spectrometry in arc heated gas environment: 1) long sample residence times and 2) the elimination of recombination reactions in the gas phase (homogeneous reaction) and along the sample probe wall (heterogeneous reaction). The ideal sampling system would deliver a sample from the source directly to the ionizer in microseconds. The sampling system developed for this work enabled the transfer of a sample from a high pressure source to the ionizer in about 0.5 s.

Probe recombination reactions were examined by the use of a theoretical model before the experimental work began. Wise and Ablow[2] developed a theoretical model to help predict ex-

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pected outlet concentrations for a sample probe that samples a stream containing a significant fraction of atoms. They examined diffusion and heterogeneous reactions for atoms flowing in a tube whose wall is catalytic. To achieve a qualitative estimate of atom recombination along a sample probe, an analytical solution presented by Wise and Ablow[2] was examined for an overall third-order reaction, the rate of which depended on the first order of atom concentration. Their solution for average atom concentration in the absence of a catalytic probe reaction at $x = L$ was

$$(n/n_0)_L = 4 \exp(\lambda\nu) * \Sigma\beta_i / [\alpha_i^2(1+\delta^2\alpha_i^2) \times (\beta_i+\nu) \exp(\beta_i\lambda)] \tag{1}$$

where $(n/n_0)_L$ is the ratio of atoms which exit the sample probe to those atoms which enter, and where

$$\beta_i = [\nu^1 + K^2 + \alpha_i^2] \tag{2}$$

$$K = k_3 M^2 R^2 / D \tag{3}$$

is the dimensionless homogeneous rate constant, and

$$\delta = 4D\,[1-\gamma/2]/\gamma c R \tag{4}$$

For δ greater than 50, α_i was approximated by finding the first root. Under this condition, the second term of the series is insignificant compared to the first term. Further, the root α_1 is related to δ by the following approximation:

$$\alpha_1^2 = 2/\delta \tag{5}$$

Since the homogeneous rate constant K is dependent upon M, many rate equations are possible. The rate constants for N_2 were chosen from Ref. 3 because N_2 is the dominant species. The rate constants used are given for the kinetic equation:

$$k_f = C_f T^n \exp(-Ea/kT) \tag{6}$$

For the third-order equation

$$r = k_f C_x C_y M \tag{7}$$

where C_x and C_y are the respective atom concentrations.

In Eq.(3), K can be approximately related to k_f in Eq. (7) by the following equation:

$$K = k_f X_y M^2 R^2 / D \tag{8}$$

The K is related to pressure when assuming that the third body concentration follows the ideal gas law and the product of the diffusion coefficient and the pressure is a constant, or

$$K = \frac{k_f P^3 R^2 X_y}{R_g^2 T^2 Dp} \tag{9}$$

Thus, K is a third-order function of pressure (since Dp is constant) and a negative second order in temperature. The lower the sample probe pressure and the higher the temperature, the less recombination will occur along the probe due to homogeneous reactions.

For our system, $R = 2 \times 10^{-3}$ m, $T = 300$ K, $Dp = 1.82$ m^2 Pa/s,[5] and $R_g = 8314$ J/(kg mole K). Choosing $X_y = 0.10$ as the approximate mole fraction of atoms of the second body in a three-body reaction, we can estimate the influence of pressure on homogeneous recombination. At pressures of 5 mbar (~4 Torr) or less, the homogeneous recombinations are negligible for a probe L/R (length to radius ratio) less than 400 for oxygen atoms to oxygen molecules, for nitrogen atoms to nitrogen molecules, and for nitrogen plus oxygen atoms to nitric oxide. As pressure increases above 5 mbar, the homogeneous recombination of nitrogen and oxygen atoms to nitric oxide becomes significant.

The influence of a catalytic wall was added to the analysis as shown in Fig. 1. Figure 1 depicts the ratio of the outlet oxygen atom concentration to the inlet concentration for a quartz probe with an oxygen atom wall recombination coefficient of 0.0002. Under a probe pressure of approximately 6 mbar, we see that the outlet atom concentration is approximately 60% of the entering sample concentration for L/R approximately equal to 250. The ideal probe would have a low L/R ratio, a low residence time (high velocity), low pressure, and zero wall recombination. To meet these specifications (especially the latter), a quartz sample tube was built.

Description of the Mass Spectrometer Sampling System

Figure 2 is a block diagram for the mass spectrometer sampling system. A sample of gas from the arc heated stream was pulled through a probe, and a solenoid valve was placed between the vacuum system and the probe. The valve allowed for remote operation of the sampling system in the control room. Following the solenoid valve were three vacuum stages that consisted of mechanical vacuum pumps separated by needle valves (Nupro SS-4H). The purpose of the vacuum pumps was to reduce the gas sample residence time from the probe tip to the mass spectrometer ionizer. The gas sample then flowed into the mass spectrometer ionizer where it was ionized. The total length of the sampling system from the tip to the ionizer was 5.4 m.

Two gas sample probes were used in this work. The first probe was a water-cooled copper tube (pitot tube) used for measuring stagnation pressure at the sampling point behind a normal shock. The pitot tube conveniently interfaced with the existing systems. The second sampling probe was a water-cooled quartz tube. A schematic of the quartz probe is shown in Fig. 3. The quartz probe was designed to allow for cooling water to pass around its tip and outside of the inner sample probe wall for a high temperature environment.

For this work, a UTI Model AMX-100 quadrupole mass spectrometer was used with a range of 0 – 100m/e and a reso-

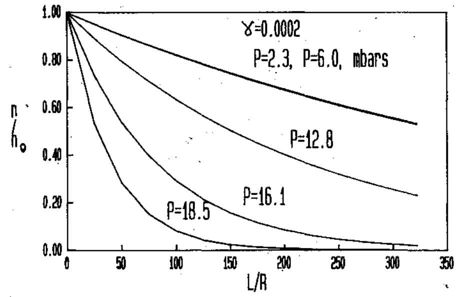

Fig. 1 **Predicted atom concentration as a function of L/R ratio for a quartz probe (γ = 0.0002, ν = 25 m/sec, T = 300 K, and P is in mbars).**

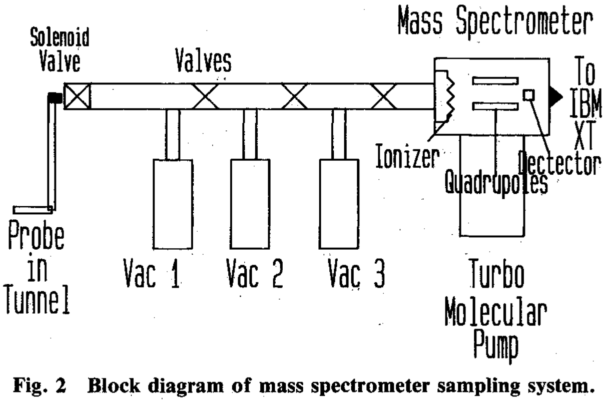

Fig. 2 **Block diagram of mass spectrometer sampling system.**

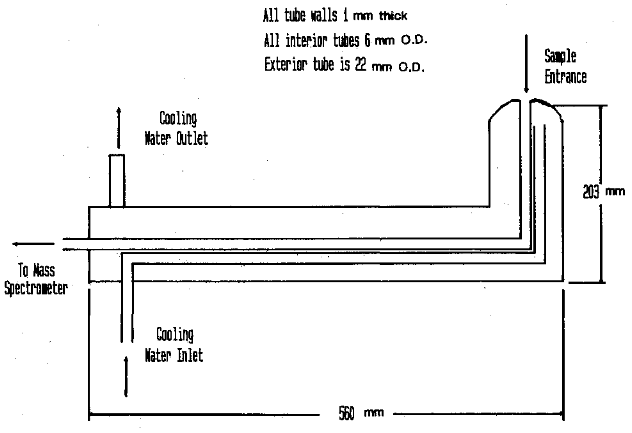

Fig. 3 Schematic diagram of the quartz probe designed for sampling gas from a heated gas flow environment.

lution of $M/\Delta M = 2M$. The quadrupole was located next to the large vacuum chamber into which the arc heater exhausted.

The electronics of the quadrupole were interfaced with an IBM-XT computer through a Cybord A/D and D/A converter (Isaac Model 91-I). An IBM-XT was used for control and data acquisition. Operating characteristics for the mass spectrometer were ionization voltage of 70 eV and filament emission currents of 0.2 – 0.4 ma. Operation pressure for the mass spectrometer averaged around 2×10^{-5} mbar. For this work, mass spectrometer signals were collected at m/e ratios of 14 (N atoms), 16 (O atoms), 17 (OH molecules), 18 (H_2O molecules), 28 (N_2 molecules), 30 (NO molecules), 32 (O_2 molecules), 40 (argon atoms), 44 (CO_2 molecules). The window was approximately $\pm\ 0.25m/e$.

Staged Vacuum System

The key to a successful mass spectrometer sampling system is the method of drawing in a sample from a 1-mbar to a 1×10^{-6}-mbar environment. A staged vacuum system was developed that enabled the sampling from atmospheric pressure to 1×10^{-6} mbar within 1 s. A staged vacuum system works on the principle that each stage draws about 1/100th of the sample in the previous stage and that each stage expands this sample by approximately 100 times. For example, the turbomolecular pump used at the mass spectrometer ionizer is capable of handling 0.027 m^3/s at 1×10^{-6} mbar. Since PQ = constant, this translates to a direct sample rate at 1 mbar of 0.027 cm^3/s.

For a 6.35-mm o.d. sample tube, 4-mm i.d., the linear velocity inside the tube is 2.1 mm/s. For a 1 m sample probe length, the sample time is 8 min (a poor response time) allowing recombination to occur. By adding an intermediate vacuum stage, which operates at 10^{-3} mbar and has a pumping rate of 0.5 1/s, the velocity in the 1-mbar section of the sample probe increases to 4 cm/s, and the residence time decreases to 25 s—a 19-fold improvement. By using a three stage vacuum system, the residence time dropped dramatically. The total length of the sample system was 5.2 m with a residence time of 0.57 s.

Quartz Probe Design

A quartz probe was built for use inside an arc heated test stream. Quartz was chosen due to its noncatalytic nature ($\gamma = 0.0002$) and high temperature resistance (softening point 1665°C). A 4-mm i.d., 6-mm o.d. tube was used, surrounded by a concentric 22-mm quartz tube for removing cooling water. Another 6-mm (o.d.) quartz tube, which delivered cooling water to the tip of the probe, was placed inside the outer tube. Figure 3 shows the overall dimensions of the quartz probe, which could be mounted onto the existing copper pitot tube for support. An orifice at the tip, 1 mm in diam, was used to maintain a low pressure in the sampling system as the atoms and molecules traveled through the probe. The probe, inside the ARMSEF vacuum chamber, was connected to the mass spectrometer by a 3.8-mm i.d. Telfon tube.

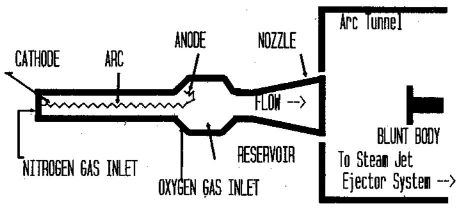

Fig. 4 Schematic of the arc heated flow system.

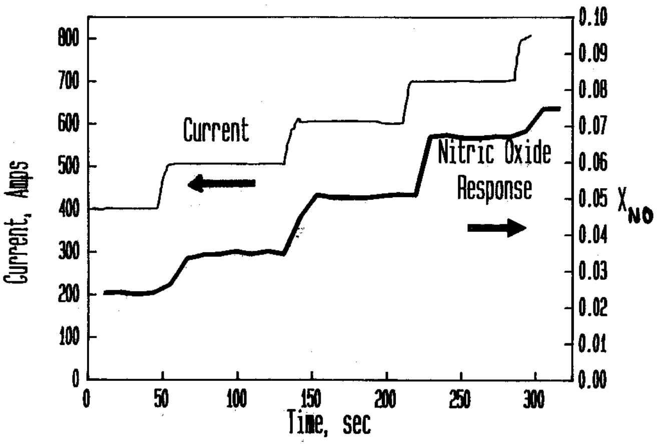

Fig. 5 Response of mass spectrometer to changes in power levels for the Cu probe.

Flowfield Conditions

The arc heater at NASA-JSC (schematic shown in Fig. 4) is used for the testing and certification of heat shield materials (i.e., Space Shuttle tiles). In order to simulate re-entry conditions, gases such as nitrogen, oxygen, argon, and combinations thereof are heated by a 1.5-m long arc column. A typical gas flow rate for this work was 0.0454 kg/s (0.1 lb/s) with 0.4 MW of energy added by the arc column (arc currents of approximately 400 A). The hot gases passed through a 5.715-cm throat and a 30-deg solid angle nozzle with an exit diameter of 38.1 cm. The arc heated gases exited the nozzle supersonically at approximately Mach 5. For these conditions, the enthalpy was about 7.2 to 7.8 MJ/kg.

For this work, variables were gas composition, probe position, arc current (enthalpy), and presence of a blunt body. The first series of measurements were for freestream species mole fractions as a function of radial and axial positions relative to the nozzle exit plane with constant gas feed composition, flow rate, and current. The second series of measurements were for freestream species mole fractions as a function of current and enthalpy at a constant probe position (centerline of the nozzle exit). Finally, the third series of measurements were for species mole fractions around a shock created by a 10.16 × 20.32 cm water-cooled copper blunt body positioned on centerline 11 cm from the nozzle exit. The full description of the JSC ARMSEF facility can be found in Ref. 4.

Response Time Evaluation

One of the objectives of this work was to demonstrate the rapid response time of a staged vacuum system for the mass spectrometer. Shown in Fig. 5 is an example of the response time for the m/e = 30 signal (nitric oxide) after step changes in current. Conditions for the run were air mass flow rate of 0.0454 kg/s and positioning centerline of the copper pitot tube at an axial position of 3 cm from the nozzle exit. Throughout the testing with the copper pitot tube, the nitric oxide signal

(m/e = 30) was an indicator of changing arc heater conditions. The signal followed the current change very closely, indicating that the overall response time was about 10 s after a current change.

Freestream Species Survey

A major objective of the work was to sample and measure atomic and molecular mole fractions as they exist in the freestream inside the vacuum chamber or arc tunnel.

Figures 6 and 7 show the measured nitrogen and oxygen atomic mole fractions as a function of pitot radial position for a gas mixture composed of 0.79 N_2 and 0.21 O_2 (air), flowing at 0.0454 kg/s, with an input current of 400 A in the arc column and a resultant enthalpy of 7.7 MJ/kg. The pitot probe sweeps across the stream at a constant axial position of 3 cm from the nozzle exit at radial increments of 2.54 cm, stopping for 60–90 s at each point to allow for adequate sampling (5 measurements per mass per point). Figures 6 and 7 demonstrate the difference in responses between the quartz probe and the copper pitot tube as sample probes. Higher atomic mole fractions for the quartz probe compared to the copper pitot tube are evident because quartz has lower wall recombination constants. For example, the recombination coefficient for O atoms on quartz is 0.0002 compared to 0.005–0.02 for copper.

The run-to-run variation for the copper pitot tube can also be seen. A check of test stream flow conditions and pressures for each run shown in Figs. 6 and 7 provide inconclusive evidence that the differences between the four runs made with the copper pitot tube could be related to flowfield conditions. Therefore, some of the variation seen in these figures are due to the day-to-day variation of conditions in the mass spectrometer sample chamber. Statistically, measurements made for O and N atoms showed that the concentration difference between the copper pitot tube and quartz probe was significant.

Also seen in Fig. 7, for the copper pitot tube, is a skewed concentration profile. Oxygen atom concentrations are lowest at the −12.7 cm radial position, peaking near the centerline and gradually leveling off as one traverses the nozzle.

Figure 8 shows the same skewness, with a maximum in the center, for the total oxygen stream fraction (oxygen contributions from O, O_2, and NO). The total nitrogen stream fraction exhibited the opposite effect; a minimum skewness occurred in the center. Total counts were constant across the nozzle exit. The arc heater is designed such that nitrogen enters at the beginning of the arc column and oxygen is added near the end of the column (this is a materials requirement in order to minimize copper electrode erosion). The skewing indicates that oxygen does not fully disperse radially as it exits the nozzle. Also, composition is dependent on radial position with more atoms observed in the center of the nozzle exit (a hotter core) compared to the nozzle sides. Subsequent heat flux probe surveys at the JSC-ARMSEF have confirmed nonuniform distribution of heat flux in the radial direction with the maximum in the center (measurements by Mr. J. Milhoan, NASA-JSC unpublished).

Figure 9 depicts results for a probe survey at an input current of 800 A and resultant enthalpy of 13.6 MJ/kg using the copper pitot tube. Once again, concentration varies with position. The N, O, NO, and O_2 concentrations all increase towards the centerline, whereas N_2 decreases at the centerline as the pitot sweeps across the nozzle. These results show higher atom concentrations than those at an enthalpy of 7.7 MJ/kg (as expected) and also a significantly higher nitric ox-

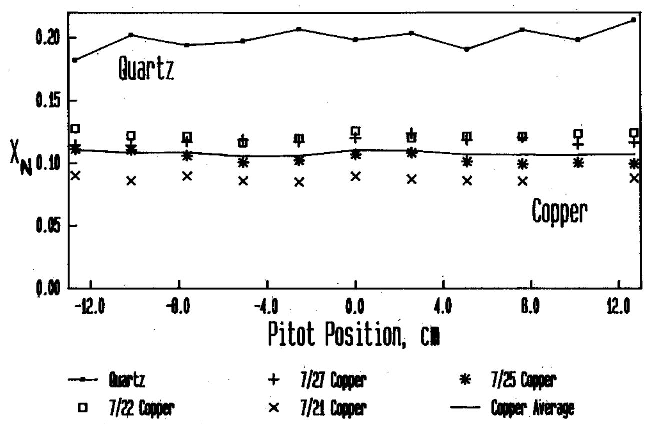

Fig. 6 Mole fraction of nitrogen atoms as a function of probe position for freestream surveys at 3 cm from the nozzle exit; air at 0.0454 kg/s and enthalpy of 7.7 MJ/kg.

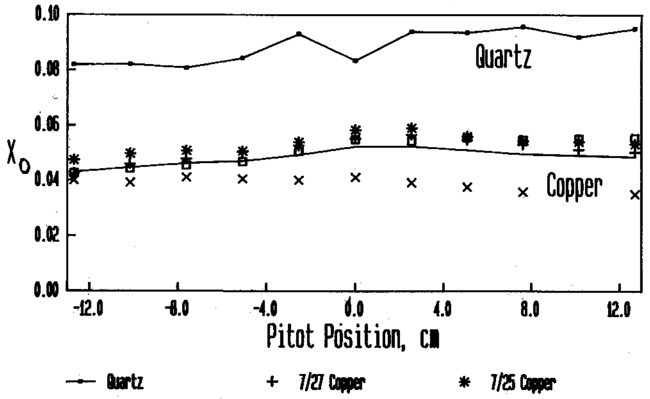

Fig. 7 Mole fraction of oxygen atoms as a function of probe position for freestream surveys at 3 cm from the nozzle exit; air at 0.045 kg/s and enthalpy of 7.7 MJ/kg.

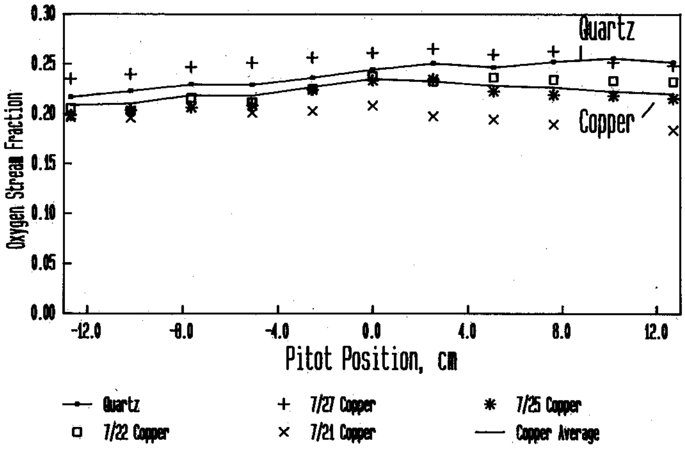

Fig. 8 Total oxygen (O_2 + O + NO) as a function of probe position for freestream surveys at 3 cm from the nozzle exit; air at 0.0454 kg/s and enthalpy of 7.7 MJ/kg.

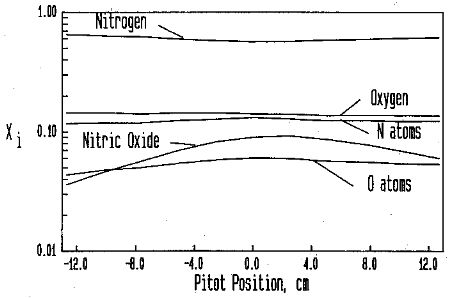

Fig. 9 Species mole fractions as a function of probe position for a freestream survey at 3 cm from the nozzle exit; air at 0.0454 kg/s and enthalpy of 13.6 MJ/kg.

ide concentration (average jump from 2 to 5%). Later work with the quartz probe showed that the majority of the nitric oxide came from recombination reactions along the copper pitot tube walls, and, therefore, nitric oxide is a relative indicator of N and O atoms present in the freestream for the copper pitot tube system. The concentration gradient seen in the radial direction indicates that more atoms exist in the core of the freestream than at the edge. Again, the concentration peaks slightly skewed right. There are two possible explanations for the skewing: pitot tube alignment and arc column alignment. Pitot tube alignment was checked daily; zero represents the true nozzle centerline pitot tube position.

As the distance from the nozzle increased, the radial profiles flattened somewhat. In a comparison of pitot sweeps of the freestream at distances of 3 and 23.3 cm from the nozzle exit, oxygen atomic mole fraction decreased from 7.8 to 5.5% for the quartz probe and from 4 to 3% for the copper pitot tube. The skewing also shifted left, although, as pointed out above, the profile is somewhat flatter. These results further imply that the frozen chemistry freestream model may be incorrect and that atom recombination is occurring in the freestream expansion after it exits the nozzle. Further verification of fewer atoms, as a function of distance from the nozzle exit, can be made by comparing nitric oxide concentration profiles. Again, the mole fraction for nitric oxide decreased from 2 to 1% for the copper pitot tube.

A series of surveys was conducted on the freestream sampling at the centerline with current (and therefore the resultant total enthalpy) as the variable. Figures 10–12 portray respective atom-mole fractions for N, O, and NO as a function of enthalpy from 7 to 17 MJ/kg with airflow rate at 0.0454 kg/s (0.1 lb/s). These results again demonstrate the catalytic nature of the copper pitot tube vs the quartz probe; atom-mole fractions for N and O are significantly lower for the copper pitot tube. Significant N atoms appear to be present in the freestream. If the quartz probe is pulling a representative sample, these results suggest that some nitrogen dissociates before all of the O_2 dissociates. A common assumption for arc heated flowfield catalysis is that the energy partition is used first to dissociate O_2, then, when all of the O_2 is dissociated, N_2 begins to dissociate. Therefore, verifications of these observations are recommended and, if verified, various arc heated flowfield models should be corrected to account for the variation.

It is interesting to note that total counts decreased as enthalpy increased. This result must be related to a larger proportion of atoms relative to molecules in both the arc heated flowfield and the mass spectrometer chamber as enthalpy increases. In the mass spectrometer chamber, the presence of molecules will increase total counts because fragments of the molecules are also counted. At lower enthalpies more molecules exist compared to atoms, and the total N_2 and O_2 fractions were relatively constant as a function of enthalpy.

Table 1 summarizes the results for species concentrations measured at the centerline with the quartz probe as a function of enthalpy (input arc currents of 400, 700, and 1000 A) and as a function of distance from the nozzle exit (3, 15.24, 23.32 cm). Table 1 serves as an overall summary of the freestream species survey of air. Results are reported on a water-free basis because water is always present in the background of a mass spectrum. The nitrogen atom-mole fraction increases as a function of enthalpy and decreases as a function of distance from the nozzle exit. The oxygen atom-mole fraction follows the same trend. The nitrogen molecule mole fraction decreases as a function enthalpy and increases as a function of distance. Oxygen molecules show an even trend with a deviation of roughly ±0.01 mole fraction.

The results support the logical conclusion that more atoms and fewer molecules exist as enthalpy increases. However, changes in atom concentration occur as a function of distance. This was unexpected and cannot, at this time, be fully explained. Therefore, we are left with the conclusion that recombination reactions are occurring in the *z* direction and that the frozen chemistry assumption must be re-evaluated. Spectroscopic verification of this finding is highly recommended.

It was also found that nitrogen atoms exist at conditions where models predict little nitrogen dissociation. Possible ex-

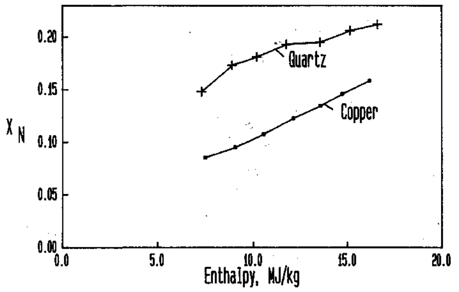

Fig. 10 **Mole fraction of nitrogen atoms as a function of enthalpy at a centerline probe position 15.24 cm from the nozzle exit; air at 0.0454 kg/s.**

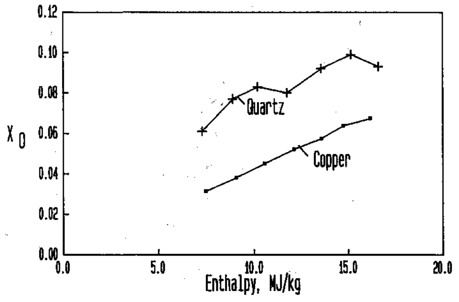

Fig. 11 **Mole fraction of oxygen atoms as a function of enthalpy at a centerline probe position 15.24 cm from the nozzle exit; air at 0.0454 kg/s.**

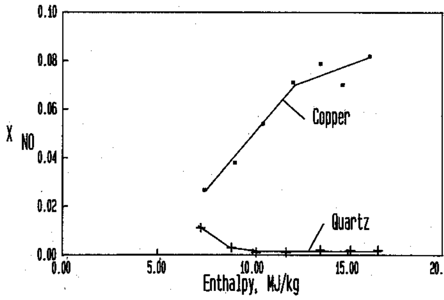

Fig. 12 **Mole fraction of nitric oxide as a function of enthalpy at a centerline probe position 15.24 cm from the nozzle exit.**

Table 1 **Freestream species mole fractions in an arc heated flowfield as a function of enthalpy and axial position for a mass spectrometer sampling system with a quartz probe**

Current, A	400	700	1000	400	400
Enthalpy, MJ/kg	7.29	11.75	16.6	7.42	7.39
z, cm (distance from nozzle exit)	15.24	15.24	15.24	3.0	23.32
Species mole fraction, centerline					
N atoms	0.144	0.192	0.209	0.205	0.112
O atoms	0.060	0.079	0.092	0.086	0.053
N_2 molecules	0.609	0.556	0.518	0.527	0.662
NO molecules	0.011	0.001	0.002	0.015	0.007
O_2 molecules	0.168	0.164	0.172	0.157	0.159
Total	0.992	0.993	0.992	0.999	0.992

NASA-JSC run number arc jet number 2-795-SD
Inlet gas mixture 0.79 N_2 and 0.21 O_2
Water free base
Quartz probe

Table 2 Species mole fractions for different gas compositions in an arc heated flowfield for a mass spectrometer sampling system with a copper pitot probe

Gas	21% O_2	11% O_2	N_2
Current, A	400	400	400
Enthalpy, MJ/kg	7.7	7.58	6.62
N atoms	0.1079	0.1449	0.1540
O atoms	0.0588	0.0252	0.0000
N_2 molecules	0.6435	0.7356	0.8349
NO molecules	0.0242	0.0039	0.0036
O_2 molecules	0.1636	0.0886	0.0052
Ar atoms	0.0020	0.0018	0.0022
NASA-JSC run number	2-757-SD	2-758-SD	2-777-SD
Water free basis			
Copper pitot probe			

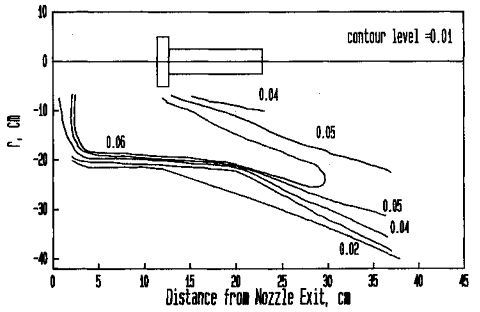

Fig. 13 Contour plot of nitrogen atom mole fractions for a shock around a blunt body; air 0.045 kg/s and enthalpy of 13.44 MJ/kg.

planations for this are that 1) nitrogen atoms are created in the arc before all of the oxygen dissociates or 2) nitrogen molecules, in excited states, are reaching the ionizer and fragmenting at a higher ratio than ground level nitrogen because the energy required for dissociation is less. Because excited nitrogen molecules have been reported in the freestream,[6] the source of the high $m/e = 14$ counts may be related to fragments from excited nitrogen molecules reaching the ionizer. It is quite possible that excited nitrogen states decrease as a function of distance from the nozzle exit. This would help explain the fall in nitrogen atoms earlier attributed to recombination in the flowfield.

Oxygen molecules are also observed where conditions predicted full oxygen dissociation. Possible explanations for this are that 1) not all of the oxygen molecules dissociate in the arc, and 2) oxygen atoms present in the arc recombine on the probe wall before reaching the ionizer. Because spectroscopically[6] no excited molecular oxygen has been reported in the freestream, the latter explanation currently has the strongest support. Further support can be seen in Fig. 1, which shows that oxygen recombination will be significant depending on the L/D and K values. Under the best conditions, only 70% of the atoms will theoretically reach the ionizer because the L/R is above 300.

Table 2 is a comparison of species measurements for different gas compositions. The measurements were made with the copper pitot tube and therefore are biased towards higher NO, O_2, and N_2 mole fractions as compared to the quartz probe due to probe wall reactions. However, the results give a relative idea of compositions for gas streams composed of mixtures other than air. Table 2 shows the expected results of more nitrogen atoms and molecules as the gas mixture changes from air to nitrogen. The presence of N atoms further suggests that nitrogen may dissociate or that some of the energy is partitioned into higher energy states of nitrogen molecules that fragment easier than ground state nitrogen molecules when they reach the mass spectrometer ionizer. Future arc heated flowfield models should include energy partitioned into higher energy levels of nitrogen molecules and nitrogen atoms.

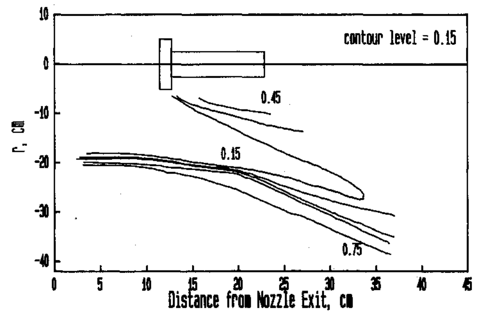

Fig. 14 Contour plot of water mole fractions for a shock around a blunt body; air 0.045 kg/s and enthalpy of 13.44 MJ/kg.

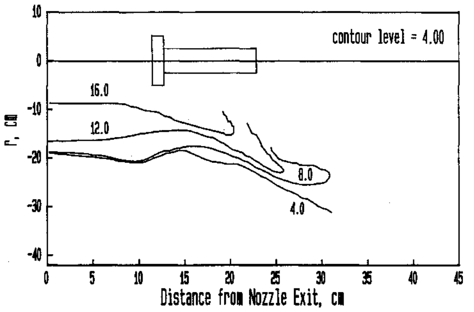

Fig. 15 Contour plot of pitot pressure readings (mbar) around a blunt body; air 0.045 kg/s and enthalpy of 13.44 MJ/kg.

Shock Layer Survey

An informative series of runs obtained species mole fractions around a shock caused by a 10.16- × 20.32-cm water-cooled copper blunt body positioned on centerline in the arc heated flowfield. A set of contour plots are shown in Figs. 13–15. The position of the shock can be seen in the high or lows observed for each species. For example, in Fig. 13, the contour plot shows a broad ridge in which N atoms follow the shock wave edge and decrease on both sides of the shock edge. Shown in Fig. 14 is the contour plot for water mole fractions, which is relatively low along the shock wave. However, the water mole fraction is relatively high in back of the shock wave and where the probe comes out of the flowfield. The reason for this is probably due to the moisture from the steam ejector system diffusing back into the test chamber outboard of the freejet flowfield. A significant signal at $m/e = 18$ (H_2O) is always present in quadrupole mass spectrometers, especially when sampling humid environments.

Figure 15 depicts a pitot pressure survey made at similar conditions as those in Figs. 13 and 14. This survey was completed six months after the original work. Relative to the blunt body position, the pressure ridge follows the atomic species ridges that in turn follow the shock. There are several other similarities such as steep pressure, species gradients near the 10-cm nozzle exit position, and a −20-cm pitot position. A difference occurs near the nozzle exit where the species concentrations diminished while the pitot pressure values did not. This may be due to the measurements taken ahead of the shock where fewer atomic species exist.

The results shown are for the copper pitot tube and, therefore, represent some atom recombination; however, the procedure demonstrates that species gradients exist and that contour mappings are possible.

Conclusions

1) Response time of less than 1 s is possible with a staged vacuum mass spectrometer sampling system.

2) Sample probe recombination reactions do occur and can be minimized by using noncatalytic probes, low sampling

pressures (below 1 mbar), low residence times, and low length to radius ratios throughout the sampling system.

3) A quartz probe is a less reactive probe than a copper pitot tube probe.

4) Remote control and data acquisition is possible for a quadrupole sampling system.

5) Oxygen and nitrogen atomic-mole fractions increase in the JSC-ARMSEF freestream as current increases.

6) Oxygen and nitrogen atomic-mole fractions decrease in the JSC-ARMSEF freestream as a function of axial distance from the nozzle, indicating that simple frozen chemistry models are invalid.

7) Skewed concentration gradients are seen at the JSC-ARMSEF nozzle exit; these gradients decrease as the axial distance is increased.

8) Gas composition measurements around a shock wave are possible and offer great potential for understanding shock layer chemistry.

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References

[1] McLafferty, F. W., *Interpretation of Mass Spectra,* W. A. Benjamin Inc., Reading, MA, 1973.

[2] Wise, H., and Ablow, C. M., "Diffusion and Heterogeneous Reaction IV. Effects of Gas Phase Reaction and Convective Flow," *Journal of Chemical Physics,* Vol. 35, No. 1, 1961, pp. 10–18.

[3] Vincenti, W. G., and Kruger, C. H., Jr., *Introduction to Physical Gas Dynamics,* Wiley, New York, 1965.

[4] Rochelle, W. C., Battley, H. H., Grimaud, J. E., Tillian, D. J., Murray, L. P., Lueke, W. J., and Heaton, T. M., "Orbiter TPS Development and Certification Testing at the NASA/JSC 10 MW Atmospheric Reentry Materials and Structures Evaluation Facility," AIAA Paper 83-0147, Jan. 1983.

[5] Welty, J. R., Wicks, C. E., and Wilson, R. E., *Fundamentals of Momentum, Heat, and Mass Transfer,* 3rd ed. Wiley, New York, 1984, pp. 488 and 781.

[6] Willey, R. J., "The Identification of Excited Species in Arc Jet Flow," NASA CR-171990, 1987.