propellant surface rotates as a solid body. Hence

$$\int_0^r T\frac{dP}{P} = \frac{\omega^2 r^2}{2R_g} \tag{19}$$

Using Eq. (17), the left side of Eq. (19) can be expressed as a function of temperature only,

$$T\frac{dP}{P} = \left(\frac{1}{2n-2}\right)\left[\frac{-2T_f T^{-2} + T^{-1}}{T_f T^{-2} - T^{-1}}\right] dT \tag{20}$$

Substituting Eq. (18) into Eq. (17) and multiplying each side by T^2 allows the left side of Eq. (20) to be integrated where $T^* = T/T_f$

$$T^* = \ln\left(\frac{1 - T^*}{1 - T_{cl}^*}\right) + \frac{\omega^2 r^2(1-n)}{T_f R_g} + T_{cl}^* \tag{21}$$

It can be shown that T^* must lie between T_{cl}^* and 1.0. Once $T^*(r)$ is obtained, the radial momentum Eq. (17) can be integrated to obtain $P(r)$. The integration can be carried out numerically from the specified P_{cl} to the desired $P(r)$

$$P(r) = P_{cl}\exp\left[\frac{\omega^2}{R_g}\int_0^r \frac{rdr}{T(r)}\right] \tag{22}$$

The properties across the propellant surface can be evaluated by substituting the $T^*(r)$ from Eq. (21) and the $P(r)$ from Eq. (22) into Eqs. (1), (14), $W = aR_gTP^{n-1}$, and $P_0 = P(T_0/T)^{\cdot\gamma/(\gamma-1)}$. In addition, the functions relating the properties along the streamlines may be evaluated at the propellant surface:

$$C(\Psi) = [R_g T_0(\Psi)]^\gamma / P_0(\Psi)^{\gamma-1} \tag{23}$$

$$E = H_0(\Psi); \quad \Gamma = \omega r^2 \tag{24}$$

Figure 4 presents some typical results for the variation of P_{ocl} with ω for end-burning motors. As ω is increased for a given P_{ocl}, the throat size required to pass the same mass flow also increases. In most cases it is desired to find the chamber conditions which will occur for a particular ω and ϵ_c. Under these circumstances, it is necessary to vary the P_g at a given ω until the desired R_t is obtained. Increasing ϵ_c, or decreasing T_f or γ, increases the pressure sensitivity of the propellant to rotation. These effects can be explained qualitatively in the following manner. Decreasing γ or T_f tends to decrease the sonic velocity of the gas, hence W_t is reduced. Increasing ϵ_c tends to increase the tangential V_t due to the conservation of angular momentum. Thus for a given ω, V_t/W_t becomes larger for increasing contraction ratio and decreasing γ and T_f of the propellant gases. As V_t increases, the effective A_t decreases. An increase in $\mathfrak{M}$ affects P_g in the same manner as a decrease in T_f or γ.

Concluding Remarks

The theory presented here permits the extension of one-dimensional flow concepts to flows which are not homentropic and homoenergetic. The solution for a particular problem depends upon the initial conditions and the nozzle geometry. Once the throat is determined, other planes in the subsonic and supersonic portions of the nozzle can be investigated, recalling that radial velocities are assumed to be negligibly small.

The effects of changing composition along a streamline may be included in a simple manner if equilibrium reactions are assumed to occur. In this case, a map of the molecular weight $\mathfrak{M}$, specific heat ratio γ, and temperature T as a function of pressure should be determined. Then, during the iteration for the throat pressure, the correct values of γ, $\mathfrak{M}$, and T can be introduced for each stream tube as determined by equilibrium calculations for the assumed pressure. The problem of flow with chemical kinetics may also be studied; however, a time integration must be made reflecting the proper nozzle geometry.

References

[1] Norton, D. J., Farquhar, B. W., and Hoffman, J. D., "An Analytical and Experimental Investigation of Swirling Flow in Nozzles," *AIAA Journal*, Vol. 7, No. 10, Oct. 1969, pp. 1992–2000.

[2] Bernstein, A., Heiser, W., and Hevenor, C., "Compound-Compressible Nozzle Flows," *Transactions of the ASME*, Sept. 1967, pp. 548–554.

[3] Pearson, H. et al, "A Theory of the Cylindrical Ejector Supersonic Propelling Nozzle," *Journal of the Royal Aeronautical Society*, London, Sec. 62, 1958, pp. 746–751.

[4] Hodge, H. J. and Segars, R. A., "Choked Flow: A Generalization of the Concept and Some Experimental Data," *AIAA Journal*, Vol. 3, No. 12, Dec. 1965, pp. 2177–2183.

[5] Norton, D. J., Farquhar, B. W., and Hoffman, J. D., "Analytical Studies of the Interior Ballistics of Spin Stabilized Rocket Motors—A Literature Survey," Rept. TM-67-1, Jan. 1967, Jet Propulsion Center, Purdue Univ.

[6] Mager, A., "Approximate Solution of Isentropic Swirling Flow Through a Nozzle," *ARS Journal*, Vol. 31, Aug. 1961, pp. 1140–1148.

[7] Lewellen, W. S., Burns, W. J., and Strickland, H. J., "Transonic Swirling Flow," *AIAA Journal*, Vol. 7, No. 7, July 1969, pp. 1290–1297.

[8] Bastress, E. K., "Interior Ballistics of Spinning Solid Propellant Rockets," *Journal of Spacecraft and Rockets*, Vol. 2, No. 3, May-June 1965, pp. 455–457.

[9] Manda, L., "Spin Effects on Rocket Nozzle Performance," *Journal of Spacecraft and Rockets*, Vol. 3, No. 11, Nov. 1966, pp. 1695–1696.

[10] B. W. Farquhar, private communication, April 1969, Boeing Co., Renton, Wash.

Reaction between Oxygen Difluoride and Diborane. I: Preliminary Results

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Introduction

Mission studies[1] have indicated that the OF_2—B_2H_6 propellant system, with a calculated maximum specific impulse (1000–14.7 psi) of 368 sec, can provide a payload capability exceeding that of F_2—H_2 and O_2—H_2 and that it has advantages in handling and space storability. Both OF_2 and B_2H_6 are storable in spacecraft, have compatible liquid range, and are hypergolic, with rather short ignition delay times, at sea level and at high altitudes. This Note discusses the results from some preliminary experiments designed to provide a qualitative understanding of the OF_2—B_2H_6 reaction. In these experiments, the partial pressures of OF_2 or B_2H_6 were 20 torr or less. The reacting mixture was studied by 1) observing it in Pyrex bulbs kept at ambient or lower temperatures, 2) determining gas composition vs time at ambient temperatures from infrared spectra, and 3) obtaining pressure-temperature relationships of an equimolar mixture at low pressures during a transient heat-up cycle (to 260°C) in a metal "reactor."

Experimental Methods and Results

The B_2H_6 (supplied by Callery Chemical Company) was purified, first, by being cooled to −195°C and pumped for H_2 removal. Then, after being warmed to −160°C (with an isopentane slush bath), it was pumped out and collected

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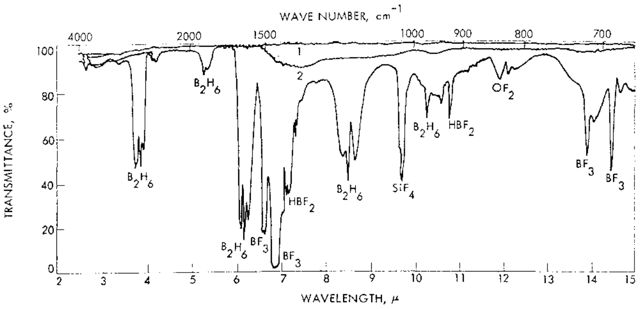

Fig. 1 Infrared spectrum of product composition with 20-torr OF_2 and 20-torr B_2H_6.

in a trap held at −195°C. No impurities could be detected from vapor pressure measurements, infrared spectroscopy, or mass spectrometry. The OF_2 (supplied by Allied Chemical Company) was purified by distillation in an apparatus described by F. J. Metz.[2] Gas density, infrared spectrometry, and vapor pressure indicated negligible impurities in the purified material. The Pyrex bulbs used for the ambient temperature experiments were made from 100-ml, round-bottom flasks. Gas pressures of 0–20 torr range were measured by a diaphragm gage (Wallace and Tiernan Inc., Catalog FA 141700), and pressures from 20 to 760 torr were measured by a Heise bourdon tube gage.

Observations from Preliminary Experiments

The preliminary investigations showed that

1) No rapid reaction occurred when B_2H_6 was added to OF_2, for the following three partial pressure combinations (in torr):

OF_2:	20	10	7.9
B_2H_6:	20	19	7.4

2) No explosive pressure-change, or other reaction, occurred when a spark was passed through a mixture of 7.9-torr OF_2 and 7.4-torr B_2H_6. In this experiment, the flask was equipped with two tungsten leads about $\frac{1}{2}$ in. apart at the center, and the spark was produced by a Tesla-coil discharge.

3) Mixtures of OF_2 and B_2H_6 exploded when a $\frac{1}{4}$-in.-diam spot on the flask was heated to glowing by a glassblower's torch. In one experiment with 7.9-torr OF_2 and 7.9-torr B_2H_6, the mixture exploded with a ping and the pressure jumped to 35 torr; in another, 20-torr OF_2 and 20-torr B_2H_6 exploded, and a yellowish-brown oily residue remained on the inside surface of the flask.

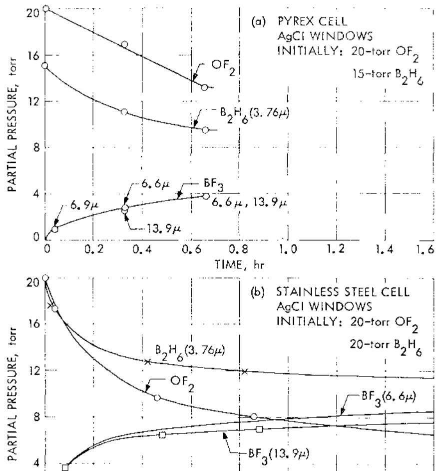

Fig. 2 Calculated concentration vs time for OF_2, B_2H_6, and BF_3 resulting from the reaction of OF_2 and B_2H_6 at ambient temperature.

Table 1 Infrared absorption peaks[a]

Compound	Wavelength of peaks, μ	Ref.
B_2H_6	3.75, 3.88, 3.92 (s); 5.25, 5.35 (m); 6.10, 6.16, 6.26 (vs); 8.32, 8.50, 8.61 (s); 10.26 (m)	5
BF_3	6.61, 6.67 (s); 6.84, 6.90 (vs); 7.22, 7.33, 7.44 (s); 13.90 (s); 14.46 (s)	6
OF_2	5.70, 5.76 (m); 10.65, 11.10 (m); 11.92, 12.10, 12.26 (s)	7
SiF_4	8.32 (m); 9.70 (vs)	
HBF_2	6.68, 6.84, 6.87 (s); 7.07, 7.12, 7.19 (vs); 8.33 (m); 10.60 (m); 10.82 (s)	8
B_2F_4	7.07 (s); 7.29 (vs); 8.65, 8.64 (vs)	9
B_2O_3	Broad, 7.5 max (s); broad, 14.0 max (m)	10

[a] m = medium, s = strong, vs = very strong.

4) When B_2H_6 was added to 20-torr OF_2, the mixture ignited and burned; a greenish flame stabilized itself at the tip of the lead-in tube (an 8-mm Pyrex tube extending to the center of the flask). This was the only example of gas-phase hypergolicity.

5) When OF_2 was inadvertently condensed on solid B_2H_6 at −195°C, no reaction was detected; the mixture exploded, however, when it began to warm up. When 5.4-torr OF_2 and 5.4-torr B_2H_6 were condensed into the tip (i.e., bottom $\frac{1}{4}$ in.) of a small cold finger about 2-mm i.d., of a 100-ml spherical flask immersed in liquid nitrogen (LN_2) at −195°C, the solid B_2H_6 coexisted with the liquid OF_2. When the LN_2 was removed, the tip warmed and exploded loudly. This result agrees with a report[3] of an explosion that resulted when liquid B_2H_6 at −169°C was dropped upon liquid OF_2 kept at −195°C.

6) To determine whether the explosive reactions described in 3 and 5 were the consequence of a low-temperature reaction forming an unstable compound, the following experiment was conducted. The OF_2 and B_2H_6 were condensed together in the tip of a cold finger cooled to −195°C; there the solid B_2H_6 was in intimate contact with the liquid OF_2. The tip was then warmed to −183°C by being immersed in LO_2. The pressure rose to 5.5 mm, corresponding to the vapor pressure of OF_2 and to the amount of OF_2 originally present (at −183°C the vapor pressure of B_2H_6 is negligible[4]). The OF_2 was pumped out, and the tip was allowed to warm to the ambient temperature (T_{amb}). The pressure rose to 5.0 torr, corresponding to the B_2H_6 originally present and showing that essentially no reaction had occurred.

7) Another experiment showed that mixtures of OF_2 and B_2H_6 can be cooled to −195°C without reaction. The neck of a 100-ml round-bottom flask was sealed off at the bottom to form a tube approximately 12 to 14-mm i.d. and 30–35 mm long. In this flask, a mixture of 5.0 torr OF_2 and 5.4 torr B_2H_6 was cooled to −195°C by total immersion in LN_2 and then allowed to warm to T_{amb}. There was no evidence of reaction as the total pressure returned to its initial value. Then the bottom 15–20 mm of the tube on the flask was cooled in LN_2 and the pressure in the flask reduced to somewhat less than 1 torr, corresponding to the vapor pressure of OF_2 at that temperature. Solid B_2H_6 was seen distributed about the cold portion of the tube. Again, when the flask was allowed to warm to T_{amb}, the total pressure returned to its initial value. Presumably, when a sufficient area of the flask is cooled, the B_2H_6 is distributed over a relatively large area as it condenses and subsequently freezes; hence only a very small amount of B_2H_6 and OF_2 are in contact.

Composition Measurements with an Infrared Spectrometer

The product composition for a typical OF_2—B_2H_6 reaction was determined from an infrared spectrum (Fig. 1) taken

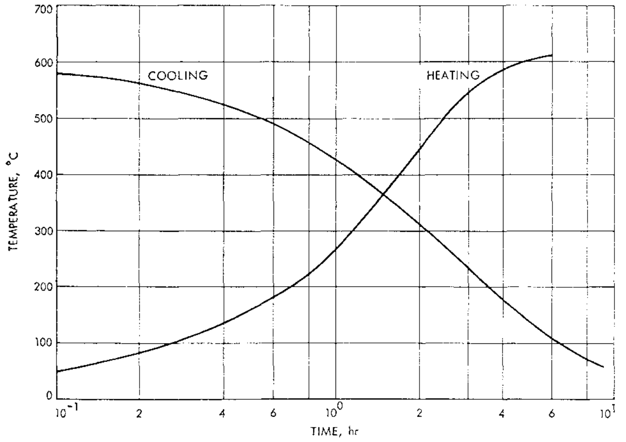

Fig. 3 Temperature vs time for heating at full power and for cooling of a nickel reactor.

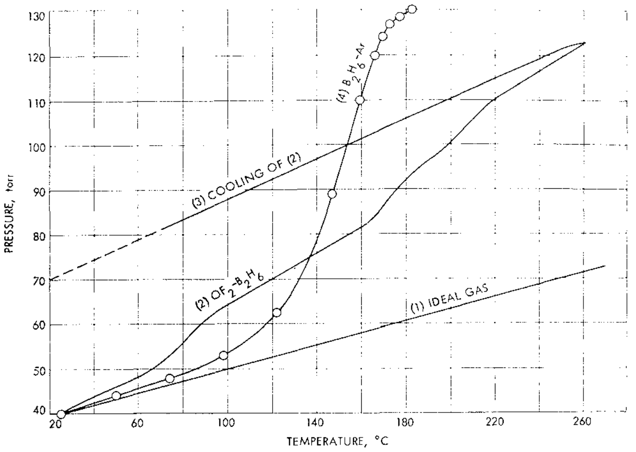

Fig. 4 Pressure-temperature relations for gas heated in a nickel reactor.

17 hr after the preparation of a 20-torr OF_2, 20-torr B_2H_6 mixture. The compounds responsible for each absorption peak were identified with the help of the literature given in Table 1.[5–10]

They included B_2H_6, OF_2, BF_3, HBF_2, and SiF_4. The SiF_4 was presumably formed either by reaction of the OF_2 with the Pyrex container during storage before the experiment, or between a product of the OF_2—B_2H_6 reaction and the wall of the infrared spectrometer cell. The BF_3 was apparently the major product, as seen from the absorption intensity of the BF_3 infrared bands. The HBF_2 arose from the reaction of BF_3 with B_2H_6.[8] After the cell was evacuated, a residual, broad, low-level absorption band, peaking at 7.5 μ, was seen (see Fig. 1) that was attributed to a film of B_2O_3 on the cell windows.

Preliminary estimates of the partial pressures of OF_2, B_2H_6, and BF_3 vs elapsed time from the addition of OF_2 to B_2H_6 are shown on Fig. 2. The partial pressures of the constituents were assumed to be proportional to their infrared absorbances. The estimation of the partial pressures of the constituents would be in error because of light scattering and pressure broadening.[11] Although pressure broadening depends upon the nature of the added gas and its pressure,[12] and for quantitative work should not be regarded as negligible, it was not accounted for here. Consequently, the estimation of the partial pressures is subject to refinement.

OF_2—B_2H_6 Reaction at Elevated Temperatures

Because a nonreacting mixture (or a mixture in which the total number of moles of volatile products were equal to the number of moles of reactants) would exhibit a linear relationship between temperature T and pressure p during heating, any noticeable deviation from linearity in $p(T)$ would indicate a reaction. In addition, the pressure measurement would show the total number of moles of gaseous species.

For a typical OF_2 and B_2H_6 mixture, $p(T)$ was obtained by heating a reactor made of $\frac{1}{8}$-in.-thick nickel, $7\frac{1}{2}$ in. long and $4\frac{1}{2}$ in. in diameter. This can had three thermocouple wells extending radially inward $\frac{3}{4}$ in. from the wall and positioned in the axial direction at the center and $\frac{1}{2}$ in. from the ends. The top and bottom were each heated by two concentric ring heaters (Chromolox ring heating elements—inner, A-00, 120 v, 200 w; outer, No. A-40, 120 v, 750 w). The sides were heated by five cylindrical band heaters (Rama-band heaters, 120 v, 45 w). This reactor was placed within a second vessel $9\frac{5}{8}$ in. in diameter by 11 in. long, and the space between was filled with insulation (Fiberfax Ceramic Blanket, XSWF, The Carborundum Co.). The voltages to the heaters were individually regulated with autotransformers. The pressure was measured by a transducer (Statham Model 11147, Spec. PA 731TC-2-350, 0–2 psia, 5 v max.) and its analog displayed, along with the thermocouple output, on an x-y recorder. The three thermocouples showed very nearly the same temperature over the entire temperature range of operation. Typical full-power heating and subsequent cooling curves for the evacuated reactor are shown in Fig. 3. It was assumed for subsequent experiments that small quantities of gas in the reactor were in thermal equilibrium with the wall.

To develop an appropriate interpretation of the state properties produced by the reaction that might occur between OF_2 and B_2H_6 at elevated temperatures, mixtures were formed with 20 torr each of the reactants, and 20 torr each of the reactant with 20 torr of inert argon. Each mixture was then subjected to the full-power heating cycle (Fig. 3). The resulting $p(T)$ curves are compared with a calculated curve for a perfect gas in Fig. 4. The curve for the OF_2—Ar mixture followed the inert gas curve, indicating that the OF_2 decomposition was negligible. However, the B_2H_6—Ar curve indicates appreciable decomposition of the B_2H_6 in the range of 120° to 170°C. The decline in the B_2H_6 decomposition rate at ~173°C is probably due to the completion of the B_2H_6 decomposition at that temperature. The B_2H_6—OF_2 reaction rate (curve 2) was somewhat greater than the rate of decomposition of B_2H_6 in the B_2H_6—Ar mixture (curve 4) in the 25° −60°C period and it was appreciably faster in the 60°–80°C period. Above ~120°C, the trend reversed. The OF_2—B_2H_6 mixture followed a complex reaction path for temperatures to about 220°C, although above that temperature the reaction appears to have nearly ceased. There does not appear to be any simple relation between B_2H_6 decomposition and the B_2H_6—OF_2 reaction. The linearity of $p(T)$ along the cooling curve indicated that there was no significant reaction during cooling and permitted an extrapolation from 74°C (where the volatile contents were withdrawn for analysis) to 25°C where the corresponding pressure for the new equilibrium composition for the reactants is shown to be 71 torr.

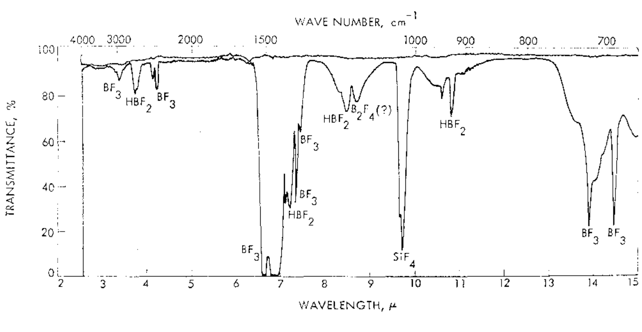

Fig. 5 Infrared spectrum from the product of reaction OF_2 and B_2H_6 heated in a nickel reactor.

To determine the composition of these noncondensable reaction products, the reactor containing the products from the OF_2—B_2H_6 reaction was opened to an evacuated bulb through a cold trap held at −195°C. A mass spectral analysis, performed by M. Frech of the Jet Propulsion Laboratory, showed that better than 99% of the material transferred to the bulb was H_2. An infrared spectrum of a sample of the constituents retained in the cold trap is shown in Fig. 5. Identifiable compounds included BF_3, HBF_2, and SiF_4. A peak at 8.7 μ was attributed to B_2F_4, but that identification was uncertain. The BF_3 was definitely the predominant reaction product. If the reaction between OF_2 and B_2H_6 were assumed to be

$$3OF_2 + 3B_2H_6 \rightarrow B_2O_3 + 2B + 2BF_3 + 9H_2,$$

then the calculated final pressure for 40-torr initial pressure would be 73.3 torr, a value very close to the observed 71 torr. The reaction equation assumed that nonvolatile boron and B_2O_3 would have been formed as products of the B_2H_6—OF_2 reaction. The presence of solid products was verified experimentally when 200 mm of F_2 was added to the evacuated reactor and heated to 600°C; the resulting gases were pumped out through a Pyrex trap, indicating the pressure of BF_3 and SiF_4 (the latter having resulted from the reaction of F_2 with the Pyrex). The BF_3 must have come from nonvolatile materials in the reactor by such reactions as

$$B_2O_3 + 3F_2 \rightarrow 2BF_3 + \tfrac{3}{2}O_2$$

and

$$B + \tfrac{3}{2}F_2 \rightarrow BF_3$$

and its existence serves to substantiate the reaction equation noted previously. The composition of the solid materials is likely to be more complex than a mixture of B and B_2O_3, and may well consist of polymeric materials containing B, H, and O. Further studies are required to determine their nature.

Conclusion

At ambient temperatures and low pressures, OF_2 and B_2H_6 react slowly to produce mostly BF_3 and probably H_2 as volatile products. Mixtures of OF_2 and B_2H_6 can coexist at −195°C, but they can also explode while warming to ambient temperature. When these compounds are heated together, nonvolatile boron compounds, along with BF_3, H_2, and smaller amounts of HBF_2 and possibly B_2F_4, are produced. The reaction of an equimolar mixture of OF_2 and B_2H_6 may be tentatively represented as

$$3OF_2 + 3B_2H_6 \rightarrow B_2O_3 + 2B + 2BF_3 + 9H_2$$

References

[1] Dawson, B. E. and Schreib, R. R., Jr., "Investigation of Advanced High Energy Space Storable Propellant System–OF_2/B_2H_6," AIAA Paper 238-63, Los Angeles, Calif., 1963.

[2] "Structural Studies of Inorganic Oxidizers," Annual Summary Report RPL-TDR-64-98, 1964, Contract AF 04(611)-9372, Midwest Research Institute, Kansas City, Mo.

[3] Dawson, B. E., Lum, A. F., and Schreib, R. R., Jr., "Investigation of Advanced High Energy Space Storable Propellant," Rept. 5507F, Contract NASw-449, June 1962, Thiokol Chemical Co., Reaction Motors Div., Denville, N.J.

[4] Stock, A., *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N.Y., 1933.

[5] Price, W. C., "The Absorption Spectrum of Diborane," *Journal of Chemical Physics*, Vol. 16, No. 9, Sept. 1948, pp. 894–902.

[6] Toy, M. S., Cannon, W. A., and English, W. D., *Solution and Conductivity Studies in Fluorine-Containing Liquid Oxidizers*, DA-31-124-ARO(D)-115, QPR-5, 1964, Astropower Lab., Douglas Aircraft Co., Newport Beach, Calif.

[7] Simons, J. H., *Fluorine Chemistry, Vol. II*, Academic Press, New York, 1954, p. 498.

[8] Coyle, T. D., Ritter, J. J., and Farrar, T. C., "Preparation and Properties of Difluorobane," *Proceedings of the Chemical Society*, Jan. 1964, p. 25.

[9] Finch, A., Hyams, I., and Steele, D., "The Vibrational Spectra of Diboron Compounds. I. Infrared Spectra of Diboron Tetrafluoride," *Spectrochimica Acta*, Vol. 21, No. 8, Aug. 1965, pp. 1423–1431.

[10] Fisher, H. D., Kiehl, J., and Cane, A., *Infrared Spectra and Thermodynamic Properties of Trifluoroboroxine (FBO_3)*, Rept. R-HTC-61-90, Contract AF 33(616)-6781, 1961, Hughes Tool Co., Culver City, Calif.

[11] Coggeshall, N. D. and Saier, E. L., "Pressure Broadening in the Infrared and Optical Collision Diameters," *Journal of Chemical Physics*, Vol. 15, No. 1, 1947, pp. 65–71.

[12] Goldstein, M. S., "The Oxidation of Diborane," PhD thesis, Feb. 1960, Rensselaer Polytechnic Institute, Chemistry Dept., Troy, N.Y.

Nonsteady Flow past Duct Junctures

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Nomenclature

D = hydraulic diameter
f = defined by Eq. (3)
h = enthalpy per unit mass
$L_{MAX}(M)$ = length of duct for steady adiabatic flow to be accelerated by friction from M to $M = 1$
M = Mach number
P = pressure; $P_{ij} = P_i/P_j$
R = radius or gas constant
T = temperature
t = time
u = velocity
x = distance
γ = ratio of specific heats
Δq = nondimensional momentum loss defined by Eq. (2)
ρ = density
τ_w = shear stress at wall

Subscripts

t = stagnation property
1,2, . . . = flow regions (indicated on figures)

Superscript

$*$ = sonic point property

1. Introduction

A VENTILATION system for an underground bomb shelter must be designed to prevent the passage of a bomb-produced blast wave into the installation. A blast valve triggered in advance of shock arrival may be used. For analyses of blast loads, a method for treating the flow in the neighborhood of duct junctures is needed. In general, this flow will be three-dimensional and viscous, and complex wave interactions will occur. However, a duct juncture is typically a small part of a duct system, and the time required to establish quasi-steady flow in the juncture is much shorter than for the ventilation system as a whole. We will assume

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