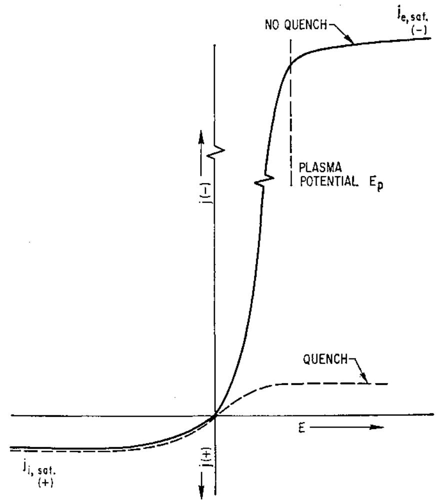

Fig. 2 Langmuir probe characteristic curves.

negative ion and electron terms, we obtain the saturation current ratio

$$\frac{j_{(-)}}{j_{(+)}} = \frac{n_e\bar{c}_e + n_{i(-)}\bar{c}_{i(-)}}{n_{i(+)}c_{i(+)}} \tag{1}$$

for a partially quenched plasma. For the case where all temperatures are approximately equal, particle velocities are inversely proportional to the square root of the molecular weights m. Thus, for a neutral plasma where $n_e + n_{i(-)} = n_{i(+)}$ and if $m_{i(+)} = m_{i(-)}$,

$$\frac{n_e}{n_{i(+)}} = \frac{(j_{(-)}/j_{(+)}) - 1}{(m_{i(+)}/m_e)^{1/2} - 1} \tag{2}$$

The mass ratio factor in the denominator typically has a value of several hundred for heavy ions; therefore, if, as has been observed, $j_{(-)}/J_{(+)}$ is of order one, it follows that $n_e/n_{i(+)} \ll 1$, and the number of electrons is reduced to a negligible value compared with positive and negative ions. Notice that, as shown in Fig. 2, little change was observed in positive saturation current, indicating no significant change of plasma ionization level.

IV. Results

Most of our tests were performed at a channel static pressure of 30 mmHg and an average velocity of about 2000 fps. The average plasma equilibrium temperature was 3300°K at the quench injector station and 2500°K at the downstream diagnostic region where the electron number density was $4(10)^{10}/\text{cm}^3$. From the many additives tested,[4] the fluorine compounds listed in Table 1 were effective midstream quenchants when added in a mass ratio to air of a few per cent or less, as indicated. Quench effectiveness was determined by a decrease in integrated n_e to less than the microwave interferometer sensitivity range, and/or a decrease of 30 to 100 in the Langmuir probe negative saturation current, so that $j_{(-)}/j_{(+)} = 1\text{–}3$. As shown in Table 1, the flush wall probe results indicate that near the cool wall, quenching was effective at mass ratios about 10 times less than the midstream values. Results were found to be independent of the injection scheme used. Operation of the channel at higher temperatures and $n_e = 3(10)^{11}/\text{cm}^3$ indicated that for these compounds quenching was not obtained in those portions of the test region profile where temperatures exceeded 3000°K. The fact that quenching was most effective near the cool wall and not at all effective in high-temperature regions indicates possible attachment to compounds only present in the flow below their dissociation level near 3000°K. Considerable experimentation was performed with water injected both as superheated steam and in liquid form. No effective quenching was noted even when the water was injected in quantities up to 15% of the air flow.

Table 1 Test results

Additive	Mass ratio	$[j_{(-)}/j_{(+)}]$ centerline	$[j_{(-)}/j_{(+)}]$, wall
SF_6 $CBrF_3$ CF_4	$3(10)^{-2}$	1 – 2	1
	$3(10)^{-3}$	∞[a]	5
C_2F_4[b]	$5(10)^{-1}$	3	1
	$2(10)^{-1}$	∞	3
NF_3[b]	$5(10)^{-3}$	2	1
	$2(10)^{-3}$	∞	2
C_2F_4[b]	$1(10)^{-2}$	3	1
	$1(10)^{-3}$	∞	2

[a] Indicates $j_{(-)} >> j_{(+)}$ (no quenching).
[b] Injection 4 in. downstream (transit length 8 in.).

It is interesting to note that, as previously mentioned, little change was noted in the probe positive saturation currents prior to and subsequent to quenching, whereas major decreases in positive current were reported for the argon tests of Ref. 1. This points out the different mechanisms responsible for quenching in the two experiments. In our tests negative charge exchange alone appeared to be dominant; the results of Ref. 1 indicate that in the argon experiments a deionization of the plasma occurred.

References

[1] Carswell, A. I. and Clouthier, G. G., "Supersonic Plasma Streams Seeded With Electronegative Gases," *The Physics of Fluids*, Vol. 7, No. 4, April 1964, pp. 602–608.

[2] Malliaris, A. C. and Libby, D. R., "Testing the Performance of Electrophilic Compounds in High Temperature Flows," AIAA Paper 68-363, San Francisco, Calif., 1968.

[3] Starner, K. E. and Spencer, D. J., "An Arc Plasma Channel for Testing of Reentry Boundary Layer Instrumentation," TR-1001(2240-10)-5, Nov. 1966, The Aerospace Corp., El Segundo, Calif.

[4] Starner, K. E., "Evaluation of Electron Quench Additives in a Subsonic Air Arc Channel," TR-0200(4240-10)-2, Sept. 1968, The Aerospace Corp., El Segundo, Calif.

[5] Mirels, H., "Subsonic Flow of Hot Gas through a Highly Cooled Channel," *AIAA Journal*, Vol. 6, No. 8, Aug. 1968, pp. 1585–1587.

[6] Jahn, R. G., "Microwave Probing of Ionized Gas Flows," *The Physics of Fluids*, Vol. 5, No. 6, June 1962, pp. 678–686.

[7] Talbot, L., Katz, J. E., and Brundin, C. L., "A Comparison Between Langmuir Probe and Microwave Electron Density Measurements in an Arc Heated Low Density Supersonic Wind Tunnel," TR HE-150-186, Jan. 1961, Univ. of Calif. Institute of Research, Berkeley, Calif.

Vibrational Energy Exchange on N_2-O_2 Collision

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RECENTLY, some studies on vibrational energy exchange of gas mixtures by using shock tube technique have been reported.[1–3] White and Millikan[4] found that small amounts of CO in N_2 represented the vibrational state of N_2 and they used CO as a tracer of N_2 in observing the vibrational relaxa-

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Received July 3, 1969; revision received August 22, 1969.

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tion of air. Taylor, Camac, and Feinberg[2] have estimated the probability of vibration-vibration (V-V) exchange in N_2-O_2 collision by using the data of White and Millikan[1] with the assumption that the coupling parameter α is equal to 0.75. Their estimate was a little lower than values calculated by the theory of Schwartz, Slawsky, and Herzfeld.[5]

The V-V probability of N_2-O_2 exchange has been measured by White[6] over the temperature range of 1000° to 3000°K and by Breshears and Bird[7] between 3500° to 4000°K. Their measured probabilities were about 20–30% of the estimation of Taylor et al. and the measured probabilities seemed to depend less on the temperature than indicated by Taylor et al.

In the present study, two mixtures of N_2-O_2-CO (69% N_2 + 30% O_2 + 1% CO and 39% N_2 + 60% O_2 + 1% CO) were used to obtain values of the probability of V-V exchange on N_2-O_2 collision. The profile of infrared emission of CO (4.7 μ) was observed over the temperature range of 1300° to 2650°K. The shock tube used in this investigation had a test section 4000 mm in length, 83 mm i.d. and a pair of CaF_2 windows were located 3500 mm from the diaphragm.

The test section and the dump tank were made of stainless steel. They were evacuated to a pressure of 5×10^{-4} torr, then flushed by the test gas at about 10 torr, and finally evacuated again to the lower pressure before each run. A leak rate of about 5×10^{-6} torr/min was achieved.

Infrared emission behind the incident shock wave was focused by means of concave mirrors on the slit of the monochrometer and then sensed by the InSb detector. The signal from it was fed into an amplifier and then into an oscilloscope. Signals from a series of three piezo transducers which were located 200 mm apart were used to determine the speed of the shock wave.

Test gases were nitrogen (purity of 99.999%), oxygen (purity of 99.9%), and carbon monoxide (purity of more than 99.9%). To purify them, they were passed through a cold trap, then mixed and stored at least 48 hr before use in three 12-liter flasks.

The relaxation equations for the mixture of N_2-O_2 can be approximated as follows:

$$-\frac{dX_N}{dt} = \left(\frac{1-c}{\tau_{NN}} + \frac{c}{\tau_{NO}}\right)X_N + \frac{c}{\tau^V}\left[\frac{1-\exp(-\theta_N)}{1-\exp(-\theta_O)}X_N - X_O\right] \qquad (1)$$

$$-\frac{dX_O}{dt} = \left(\frac{c}{\tau_{OO}} + \frac{1-c}{\tau_{ON}}\right)X_O + \frac{(1-c)}{\tau^V}\frac{\exp\theta_O}{\exp\theta_N}\left[\frac{1-\exp(-\theta_O)}{1-\exp(-\theta_N)}X_O - X_N\right] \qquad (2)$$

Here, $X = 1 - E/\bar{E}$ (E is the local vibrational energy and $\bar{E}$ is the vibrational energy at equilibrium with translational temperature T), $\theta = h\nu/kT$, c is the mole fraction of O_2 in the mixture and subscripts N and O denote the characteristic values of N_2 and O_2, respectively. τ_{NN} and τ_{NO} are the vibrational relaxation times of N_2 by translation-vibration (T-V) process with the collision partner of N_2 and O_2, respectively. τ_{OO} and τ_{ON} are those of O_2 with the collision partner of O_2 and N_2, respectively, and τ^V is the relaxation time of N_2-O_2 system by V-V exchange.

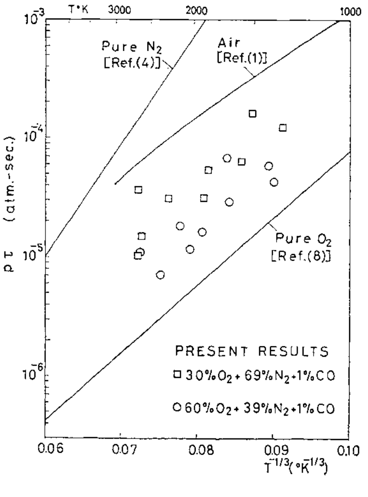

Fig. 1 Vibrational relaxation times of N_2, O_2, and their mixtures.

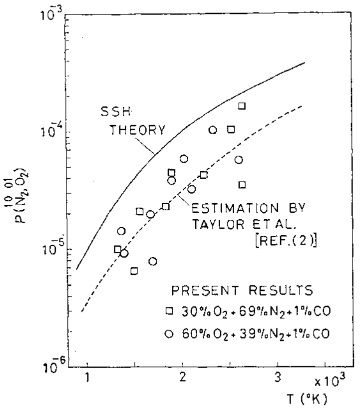

Fig. 2 Probability of vibration-vibration exchange on N_2-O_2 collision.

In the preceding equations, the cross terms in $X_N X_O$ were neglected since X_N and X_O are very small at large distances from the shock front. Equations (1) and (2) can be solved with the initial conditions, $X_N = X_O = 1$ at $t = 0$, and with the assumption that $\tau_{OO} = \tau_{ON}$ and $\tau_{OO}^{-1} \gg (1-c)/\tau_{NN} + c/\tau_{NO}$.[3] Then the following relation can be obtained:

$$\tau^V = [f_2\tau_f - (f_1 + f_2)\tau_{OO}](1 - \tau_{OO}/\tau_f)^{-1} \qquad (3)$$

where

$$f_1 = (1-c)\,\frac{\exp\theta_O - 1}{\exp\theta_N - 1},\; f_2 = c\,\frac{1-\exp(-\theta_N)}{1-\exp(-\theta_O)}$$

and τ_f if the final vibrational relaxation time of gas mixture.

In this study, the emission profiles of CO were distorted near the shock front by the effect of the V-V exchange, but log X vs time gave a good straight line correlation at large distances from the shock front. As Sato, Tsuchiya, and Kuratani[3] have interpreted analytically, each component in the mixture has the same value for τ_f, so it can be determined by observing the profile of the vibrational relaxation on CO. According to the result in Ref. 3, in which V-V probabilities on CO-N_2 and CO-O_2 exchange were obtained, the final relaxation time of N_2-O_2 mixtures may be assumed to be undisturbed by the existence of small amounts of CO. The method of transforming laboratory relaxation time to particle one was the same as used by Taylor et al.[2] The relaxation times of N_2, O_2, and their mixture are summarized in Fig. 1, where the straight lines for the relaxation times of N_2, O_2, and air are the data from Ref. 4, Ref. 8, and Ref. 1, respectively. The vibrational relaxation time of O_2 on O_2-O_2 collision (τ_{OO}) has been obtained in many papers, but the analysis of the data in this study was based on the results of Ref 8. The transition probability of V-V exchange can be obtained by the following relation:

$$\overset{10\ 01}{P(N_2,O_2)} = (\tau^V Z n)^{-1} \qquad (4)$$

where, Z is the frequency of N_2-O_2 collision and n is the number density of the mixture.

In Fig. 2, the experimentally determined probabilities are compared with the SSH theory. The present result is a little lower than the theory but the temperature dependency seems to agree well. Present results agree also with the estimation of Taylor et al. This suggests that the assumption made in their analysis is valid, namely that the extent of V-V coupling for the various systems of diatomic-diatomic collision can be estimated by knowing the vibrational energy difference of the colliding pair.

References

[1] White, D. R. and Millikan, R. C., "Vibrational Relaxation in Air," *AIAA Journal*, Vol. 2, No. 10, Oct. 1964, pp. 1844–1846.

[2] Taylor, R. L., Camac, M., and Feinberg, R. M., "Measurements of Vibration-Vibration Coupling in Gas Mixtures," *11th Symposium on Combustion*, The Combustion Institute, 1967, pp. 49–65.

[3] Sato, Y., Tsuchiya, S., and Kuratani, K., "Shock Wave Study of Vibrational Energy Exchange Between Diatomic Molecules," *The Journal of Chemical Physics*, Vol. 50, 1969, pp. 1911–1919.

[4] Millikan, R. C. and White, D. R., "Vibrational Energy Exchange Between N_2 and CO. The Vibrational Relaxation of Nitrogen," *The Journal of Chemical Physics*, Vol. 39, 1963, pp. 98–101.

[5] Schwartz, R. N., Slawsky, Z. I., and Herzfeld, K. F., "Calculation of Vibrational Relaxation Times in Gases," *The Journal of Chemical Physics*, Vol. 20, 1952, pp. 1591–1599.

[6] White, D. R., "Shock-Tube Study of Vibrational Exchange in N_2-O_2 Mixtures," *The Journal of Chemical Physics*, Vol. 49, 1968, pp. 5472–5476.

[7] Breshears, W. D. and Bird, P. F., "Effect of Oxygen Atoms on the Vibrational Relaxation of Nitrogen," *The Journal of Chemical Physics*, Vol. 48, 1968, pp. 4768–4773.

[8] White, D. R. and Millikan, R. C., "Vibrational Relaxation of Oxygen," *The Journal of Chemical Physics*, Vol. 39, 1963, pp. 1803–1806.

Laminar Boundary Layers with Zero Wall Shear, Large Suction, and Strong Adverse Pressure Gradients

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The solutions to the equations for similar laminar boundary layers with zero wall shear have been developed by several authors.[1,2] Most recently, Fox[3] has performed numerical calculations for these so-called "separated profiles" when blowing or suction is present at the wall. In constructing the solution for large suction, Fox confirmed the early result of Prandtl[4] that the pressure gradient parameter must be proportional to the square of the suction rate in order that the wall shear be zero. In an attempt to find the constant of proportionality and to develop higher-order corrections, Fox simply patched together (at a somewhat arbitrary location) the asymptotic expansion for large values of η with the convergent series expansion valid near the wall. The result derived using this procedure appears to contain an error in functional form as will be seen below.

In the present Note a more formal asymptotic expansion procedure is used to develop solutions with large suction when the wall shear is absent. Besides providing a theoretical analogue to Fox's numerical results, the present calculation is interesting because it deals with solutions for large negative values of the pressure gradient parameter. Little is known about the properties of such solutions beyond that given by the strictly numerical results of Libby and Liu,[5] Steinauer,[6] and Rogers[7] in the absence of wall mass transfer.

The describing equations and boundary conditions are[3]

$$f''' + ff'' + \beta(g - f'^2) = 0 \tag{1a}$$

$$g'' + fg' = 0 \tag{1b}$$

subject to

$$f = f_w, f' = 0, f'' = 0, g = g_w \text{ at } \eta = 0 \tag{1c}$$

$$f' = 1, g = 1, \eta \to \infty \tag{1d}$$

where the independent variable is the usual similarity variable η.

There are six boundary conditions for this fifth-order system which, however, contains the parameter β, considered here to be unknown. Hence one aspect of the ensuing calculation will be to find the functional relationship, $\beta = \beta(\mathcal{E})$, where the asymptotic parameter will be $f_w = \mathcal{E}^{-1} \gg 1$.

It is convenient to apply the elementary transformation $f = \mathcal{E}^{-1} + F$ in order to place the parameter $\mathcal{E}$ in the equations rather than in the boundary conditions. The resulting system is

$$F''' + (\mathcal{E}^{-1} + F)F'' + \beta(\mathcal{E})(g - F'^2) = 0 \tag{2a}$$

$$g'' + (\mathcal{E}^{-1} + F)g' = 0 \tag{2b}$$

subject to

$$F = F' = F'' = 0, g = g_w, \text{ at } \eta = 0 \tag{2c}$$

$$F' = 1, g = 1, \text{ at } \eta \to \infty \tag{2d}$$

A solution based on the limit process η fixed, $\mathcal{E} \to 0$ will be constructed first. Assuming that the basic functional relationship $\beta \sim f_w^2 \sim \mathcal{E}^{-2}$ given by Prandtl and confirmed by the numerical analysis of Fox is correct (subsequent calculations verify this point), we consider as the basic approximation to Eqs. (2a) and (2b) for $\mathcal{E} \ll 1$

$$g_0 = F'^2_0 \tag{3a}$$

$$g'_0 = 0 \tag{3b}$$

These equations produce solutions which are capable of satisfying boundary conditions only for large η. It also may be observed that there are no higher-order corrections. Hence the complete outer solutions are simply

$$g \sim 1, F' \sim 1$$

The outer limit process leads only to a trivial result.

In order to develop the complete structure of the boundary layer there must be used another limit process whose form is suggested by applying Eq. (2a) at the surface $\eta = 0$ to show that $F'''(0) = -\beta(\mathcal{E})g_w$ and hence that in the vicinity of the wall there must be a balance of viscous and pressure gradient forces. The transformations

$$H = F\mathcal{E}^{-1}, s = \eta\mathcal{E}^{-1}, G = g$$

lead to the desired formulation. Assuming in addition that $\beta = K_0\mathcal{E}^{-2} + K_1\beta_1(\mathcal{E}) + K_2\beta_2(\mathcal{E}) + \ldots$, where

$$\lim_{\mathcal{E}\to 0} \mathcal{E}^2\beta_1(\mathcal{E}) = 0, \lim_{\mathcal{E}\to 0} (\beta_{n+1}/\beta_n) = 0$$

and where the K_n are to be determined, we find the basic equations are

$$H''' + (1 + \mathcal{E}^2H)H'' + [K_0 + K_1\mathcal{E}^2\beta_1(\mathcal{E}) + K_2\mathcal{E}^2\beta_2(\mathcal{E}) + \ldots](G - H'^2) = 0 \tag{5a}$$

$$G'' + (1 + \mathcal{E}^2H)G' = 0 \tag{5b}$$

$$H = H' = H'' = 0, G = g_w \text{ at } s = 0 \tag{5c}$$

$$H' = 1, G = 1, s \to \infty \tag{5d}$$

where Eqs. (5d) are derived from a matching condition

Received August 27, 1969; revision received October 10, 1969. This research was supported under Project THEMIS and sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research under Contract F44620-68-C-0010. The authors express their appreciation to P. Wu who carried out the numerical calculations.

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