Supersonic Gas Sampling Error in Atmospheric Ozone Depletion Studies

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The problem of sampling trace gas concentrations in the atmosphere with a pitot-type probe moving at supersonic speed is investigated. Under certain conditions, the gas mixture entering the probe will undergo a change in concentration ratio caused by a molecular separation effect in the probe stagnation zone and this will result in an error between the measured and actual gas concentration. Using a correlation for maximum probe separation effect with flow conditions for any gas mixture, it is estimated that significant errors of this type will be introduced at altitudes in excess of 30 km. Also, it is shown that the error when sampling Freon-air mixtures will be several times greater than for light gas mixtures with air.

Introduction

OVER the past 5 years there has been increasing scientific interest in current and future levels of pollutant gases in the stratosphere. This is primarily because the existence of certain gases in this region may result in their combing chemically with ozone (O_3), thereby reducing the ozone layer, which protects animal tissue from harmful utlraviolet rays emitted by the sun.

Of the many excellent publications on this most complex problem, the report by the Australian Academy of Science (1972)[1] and that by Hoffert and Stewart (1975),[2] in which a comprehensive review of current literature on this subject has been made, are of particular interest here and form an excellent background to this paper. These authors (and others) are forced to conclude that the task of accurately predicting the degree of contamination by pollutant gases from high-altitude aircraft engine emissions and other sources theoretically is impossible, even by modern computational methods. Thus, the only way of obtaining accurate data must be by measuring the constituent gases in the atmosphere. Some atmospheric gas sampling programs have already been carried out, e.g., by Hard,[3] and more are currently in progress, involving high-altitude balloons, aircraft, or rockets. However, for systematic monitoring of the upper atmosphere over long distances, high-altitude aircraft or rockets traveling at high speed must be used. Furthermore, if supersonic transport (SST) aircraft operate over air routes in the stratosphere, then it would be highly desirable to fit these aircraft with gas sampling equipment in order to monitor their flight routes for pollutant gases. Another future source of ozone destroying pollutants will be from space shuttle vehicles, and here again some gas analyzing monitoring technique may also be required.

The problem of high-speed gas sampling in a rarefied atmosphere inevitably involves the question of how the constituents of a gas mixture flowing into a sampling probe are affected by the bow shock at the probe tip, since it is well-known that molecular separation can occur in these conditions. When this does occur, the measurement of gas constituents in a mass spectrometer within an aircraft will not represent the concentration of these constituents in the freestream; therefore, the accuracy of such measurements will be in question. It has been estimated[4] that a reduction of ozone concentration in the atmosphere by as little as 1% will seriously increase the harmful effects of ultraviolet radiation; consequently it can be seen that these measurements must be carried out with a high degree of accuracy. In this paper, an attempt has been made to estimate the maximum error possible when sampling the various trace gases (which form the known pollutants causing destruction to the ozone layer) by a probe traveling at supersonic speed at various altitudes.

Received Feb. 6, 1976; revision received June 4, 1976.
Index categories: Rarefied Flows; Supersonic and Hyersonic Flow; Atmospheric, Space and Oceanographic Sciences.

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Molecular Separation Effects in a Supersonic Sampling Probe

When a low-density gas mixture flows with supersonic speed onto an aligned pitot-type sampling probe, the disturbance set up in the stagnation zone (bounded by the probe tip and the bow shock) produces molecular separation. This phenomenon is shown schematically in Fig. 1, in which the flow paths for the heavy and light constituents in a binary mixture are qualitatively indicated. It can be seen that due to the variation in the flow paths for each molecular species, there is an enhancement of the heavier species in the sampling probe.

Reis and Fenn[5] first discovered this effect when probing a low-density free expansion jet. They found that the extent of separation achieved depended mainly on molecular weight difference and Knudsen number. To date, most experimental studies have concentrated on the possible exploitation of this effect for deliberate gas separation processes.[6,7] However,

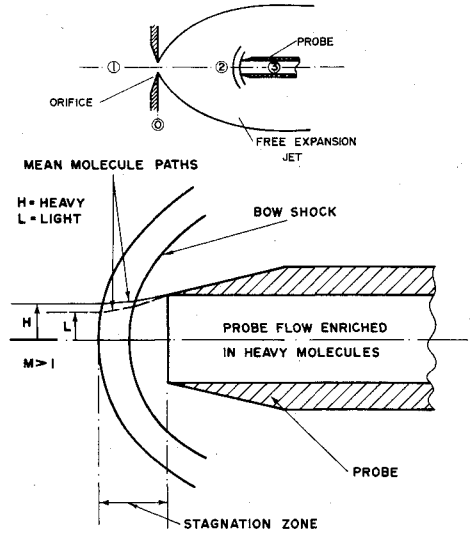

Fig. 1 Bow shock probe entrance conditions.

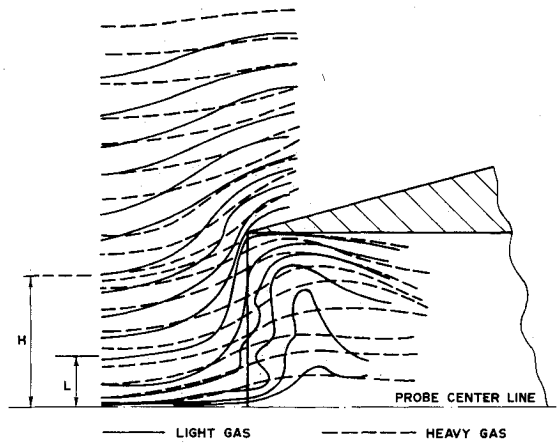

Fig. 2 Computed mean particle paths for light and heavy gas molecules at the entrance to a sharp nosed tubular probe $(n_H)_2 = 0.2$, $(\mathrm{Kn})_2 U_0/U_2 = 0.0754$.

more recently, a method of correlating the separation effect for any binary gas mixture has been introduced by Guy.[8] This study included results of a Monte Carlo method numercial computation for the case of 20% argon-80% helium flowing at a Knudsen number $(\mathrm{Kn})_2$ of about 0.15 and a Mach number M_2 of 10, impinging upon a sharp-nosed probe. The molecular flow paths resulting from this computation (which gave an indication of the successful correlation parameter) are shown in Fig. 2. Extremely sharp curvature in the light species flow path clearly shows why the heavy species is enhanced in the probe flow. This curvature is produced by a strong outward diffusion current caused by a radial pressure gradient within the stagnation region. The separation effect which is not greatly affected by the freestream Mach number above 3.0, has been shown experimentally[5,6,8] to depend also on the probe pressure. For example, if the probe pressure is less than the freestream pressure, then there will be no bow shock and hence no stagnation zone molecular separation. Conversely, if the probe pressure is the same as the stagnation pressure, there will be no flow in the probe. Thus the optimum probe pressure for gas separation occurs at probe pressures between these extremes. Since we are concerned here with the maximum possible separation effect, it is assumed that the optimum probe pressure for molecular separation is used.

The binary gas mixture correlation in Ref. 6 was for the maximum gas separation parameter

$$c_\alpha = (\alpha_3 - 1)/(\alpha_m - 1) \tag{1}$$

plotted against the freestream gas flow conditions $(\mathrm{Kn})_2 U_0/U_2$ as in Fig. 3. Subscript numbers are defined in the inset diagram of Fig. 1, and refer to various gas conditions in a free expansion jet and within the probe. α_3 is the probe gas separation factor given by

$$\alpha_3 = \frac{(n_H)_3}{1-(n_H)_3} \times \frac{1-(n_H)_2}{(n_H)_2} \tag{2}$$

in which n_H refers to the concentration ratio of the heaviest molecule type in a binary mixture and subscripts 2 and 3 refer to the freestream gas just ahead of the probe and that in the probe flow, respectively. The normalizing separation factor in Eq. (1), α_m, is the simple diffusion separation factor given by

$$\alpha_m = (m_H/m_L)^{1/2} \tag{3}$$

in which m_H is the molecular weight of the heavy species and m_H that for the light species.

The flow condition parameter in Fig. 3, $(\mathrm{Kn})_2 U_0/U_2$, consists of the Knudsen number in the freestream just ahead of the probe $(\mathrm{Kn})_2$ and the freestream velocity U_2 that is normalized by a characteristic velocity U_0. Since all the experiments in Ref.6 were carried out in a free expansion jet (as shown in the inset of Fig. 1), the normalizing velocity U_0 is given by the acoustic velocity at the expansion throat or orifice. However, the correlation is still applicable to any supersonic flow so long as the freestream Mach number and temperature conditons at the probe, M_2 and T_2 are known. The method of obtaining U_0 once U_2 has been calculated is as follows: first estimate the equivalent distance along the free expansion jet centerline to obtain M_2 (e.g., Ref. 9) and at this distance the temperature ratio T_2/T_1 can be obtained from the one-dimensional flow relationship

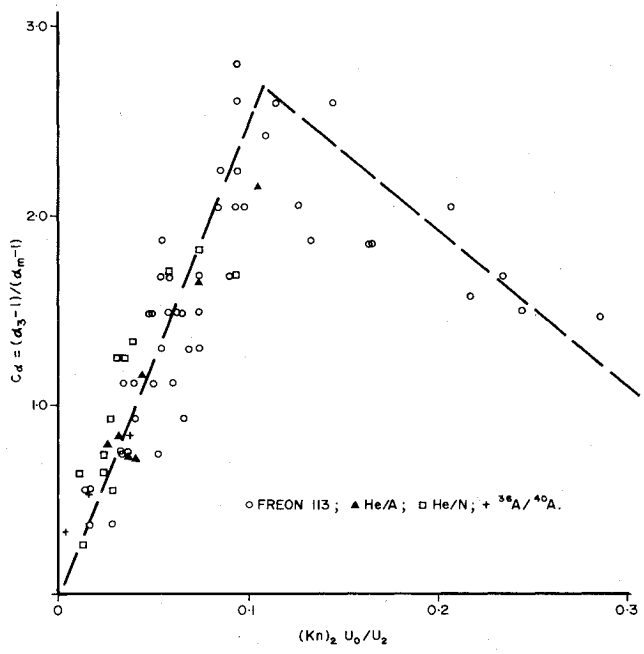

Fig. 3 C_α correlation with flow condition $(\mathrm{Kn})_2 U_0/U_2$ in the mean molecular weight range $m = 7.6$-187.

$$T_2/T_1 = \left(1 + \frac{\gamma - 1}{2} M_2\right)^{-1} \tag{4}$$

where T_1 is the stagnation temperature in the stationary gas ahead of the free jet orifice and γ is the specific heat ratio. However, the required temperature is that at the orifice, T_0, and this is given by the choked jet relationship $T_0/T_1 = 2/(\gamma + 1)$ from which U_0 or the acoustic velocity at the throat is obtained from $(\gamma R T_0)^{1/2}$ where R is the gas constant.

The Knudsen number $(\mathrm{Kn})_2$ is given as a function of pressure by the standard kinetic theory expression

$$(\mathrm{Kn})_2 = \frac{R T_2 M'}{\pi P_2 \sigma^2 d (2)^{1/2}} \tag{5}$$

where M', σ, and d are molecular mass, molecular diameter, and probe outside diameter, respectively. Since all the gas mixtures to be considered consist predominantly of air we may simplify Eq. (5) by substituting the correct values of R, M', and σ for air. Also we select a probe diameter d of 1 cm. Therefore

$$(\mathrm{Kn})_2 = (T_2/P_2)\, 26.5 \times 10^{-4} \tag{6}$$

Returning now to the correlation shown in Fig. 3, we see that initially the parameter C_α varies in a straight line relationship with $(\mathrm{Kn})_2 U_0/U_2$, according to the slope

$$\Delta(C_\alpha)/\Delta(Kn_2 U_0/U_2) \simeq 25/1 \tag{7}$$

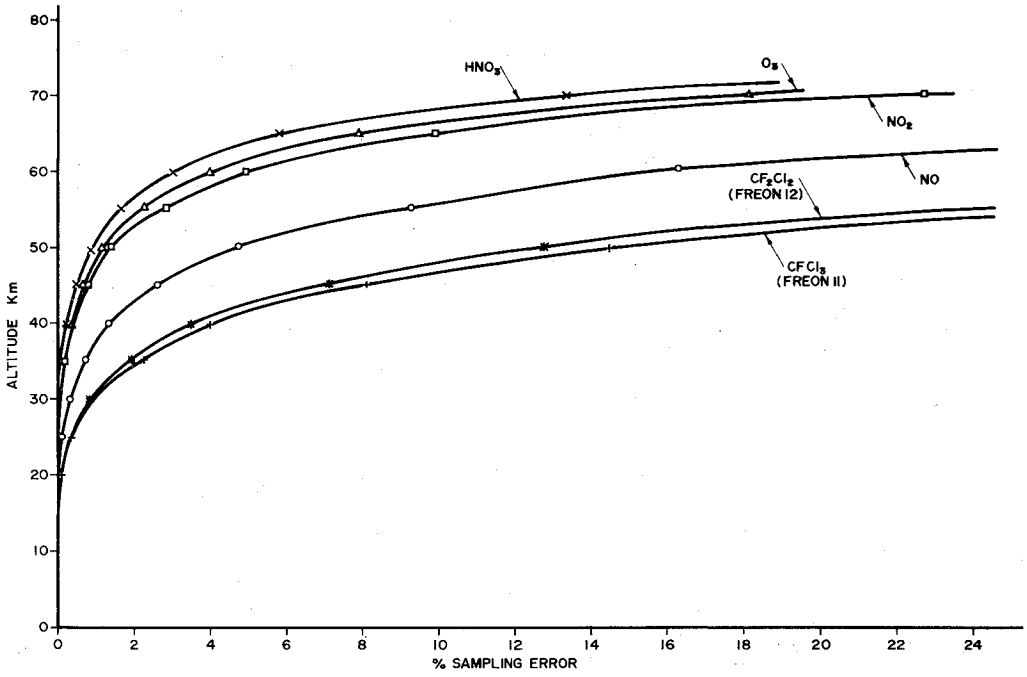

Fig. 4 Variation in trace gas concentration measurement error with altitude for several trace gas-air mixtures.

until $(Kn)_2 U_0/U_2$ attains a magnitude of about 0.11. Then the separation effect begins to decline with further increase in $(Kn)_2 U_0/U_2$. This is because the gas now becomes too rarefied to produce a strong radial diffusion current in the probe stagnation zone. However, we need not be concerned with the change of slope region in the correlation, since even at an altitude of 70 km the magnitude of $(Kn)_2 U_0/U_2$ is only 0.076 which is well within the initial straight line portion. Therefore, from the definition of C_α in Eq. (1), an approximate empirical relationship for the percentage separation in the probe gas is given by

$$(\alpha_3 - 1) = 25[(m_H/m_L)^{1/2} - 1](Kn)_2 U_0/U_2 \times 100 \qquad (8)$$

This represents the maximum precentage error in concentration measurement (using a pitot-type probe) caused by separation of the gas mixture at the probe entrance.

Results for the Variation in Sampling Error with Altitude for Trace Gas Mixtures with air

There is a wealth of information available on the variation of pressure and temperature with altitude, therefore, the variation in $(Kn)_2$ with altitude (based on a 1-cm-diameter probe) can easily be estimated. Using the U.S. 1962 standard atmosphere midlatitude and midseason temperature distribution, the $(Kn)_2$ variation with altitude shows immediately that the magnitude of $(Kn)_2$ remains small until the altitude is greater than say 30 km. We would therefore expect very little probe separation effect at altitudes lower than this.

The percentage error in the gas analysis measurement caused by the probe separation effect has been estimated for the following gas mixtures: NO + air; NO_2 + air; O_3 + air; NHO_3 + air; Freon 11 ($CFCl_3$) + air and Freon 12 (CF_2Cl_2) + air. As mentioned before, since the atmospheric concentration of all these gases is extremely small, the properties of air, at the appropriate temperature and pressure coresponding to a particular altitude, have been used in Eq. (8). However, in this equation the molecular weight of the heaviest gas in any binary mixture has been used as the value for m_H and that of the lightest gas as the value for m_L. Furthermore, as mentioned earlier, it has previosuly been shown experimentally[9] that the separation effect is almost independent of Mach number for Mach numbers M_2 above 3.0. This can also be shown theoretically according to Eq. (8) since, particularly for $\gamma \leq 1.4$, the ratio U_0/U_2 will be virtually constant for $M_2 > 3.0$. Therefore all the calculations carried out here are for a probe Mach number of 3.0.

The estimated gas sampling errors due to probe separation for the aforementioned gas mixtures are shown in Fig. 4 for a range of altitudes up to 70 km. As expected, the error is small for all the gas mixtures at altitudes less than 20 km. However, due to the larger molecular weight difference between the freons and air, these gas mixtures exhibit a much greater sampling error than any of the other mixtures. Nitrogen oxide (NO),although displaying less than half the Freon error, does, however, have more than double the error of the other light gas mixtures. For altitudes above 45 km, the sampling error is seen to become significant for all these gas mixtures, increasing rapidly with further increase in altitude.

Discussion and Conclusion

It would appear from the results of Fig. 4 that the probe sampling error due to molecular separation will be insignificant at altitudes below 20 km. Both the Concorde, TU144, and the U.S. advanced SST aircraft are intended for operation below this altitude and therefore pitot-type gas sampling probes in these aircraft should be free from molecular separation effects. However, it is obvious that very large errors will result at altitudes approaching 50 km particularly for Freon-air mixtures. At this altitude also, the estimated error of 0_3 air measurement is greater than 1%, which is significant since the ozone number density is still quite large at this height. The effect of eddy diffusion in the atmosphere has been shown to be a significant mechanism for transporting ozone-depleting pollutants into the upper atmosphere, whereas, the possible upper atmospheric emission of space shuttle and hypersonic transport exhaust gases further points to the necessity to monitor these regions.

In conclusion, therefore, this study shows that SST aircraft should be able to carry out atmospheric gas sampling at supersonic speeds without significant errors due to molecular separation. Pitot-type sampling probes used at supersonic speeds and at altitudes above 30 km will, however, give rise to molecular separation errors.

Finally, the problem investigated in this study applies to any similar situation of low-density gas analysis at supersonic speeds such as in low orbiting interplanetary probes, where it is easy to visualize that quite severe gas sampling errors may

result from probe separation effects. These errors may be overcome in several ways. For example, a) large probe diameter will reduce the Knudsen number, b) low probe pressure will ingest the bow shock (although this is likely to lead to molecular separation internally at the mass-spectrometer inlet, and c) a set of calibrated corrections can be used to off-set the probe induced measurement errors.

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