

Technical Notes

TECHNICAL NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes cannot exceed 6 manuscript pages and 3 figures; a page of text may be substituted for a figure and vice versa. After informal review by the editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Non-Arrhenius NO Formation Rate in One-Dimensional Nozzle Airflow

G. Colonna,* M. Tuttafesta,[†] and M. Capitelli[‡]
Consiglio Nazionale delle Ricerche, 70126 Bari, Italy
and
D. Giordano[§]
ESA, 2200 AG Noordwijk, The Netherlands

Nomenclature

A	= cross-sectional nozzle area
c_i	= mass fraction of the i th species
c_{iv}	= mass fraction of the i th species in v th vibrational level
c_p	= global constant pressure specific heat
c_{pi}	= molar constant pressure specific heat for i th species
c_s	= speed of sound
h_i	= formation enthalpy for the i th species
h_T	= translational and rotational enthalpy per unit mass
h_v	= internal enthalpy per unit mass
M	= Mach number
m	= mean molar mass
m_i	= molar mass for i th species
P	= pressure
R	= universal gas constant
R^*	= R/m
T	= gas temperature
T_i	= vibrational temperature of the i th species
u	= flow speed
x	= position
α	= c_p/R
α_i	= c_{pi}/R for i th species
γ	= c_p/c_v
ϵ_{iv}	= molar energy of v th vibrational level of the i th species
ρ	= global mass density
ρ_{iv}	= mass density of the i th species in the v th vibrational level
$\dot{\rho}_{iv}$	= source term caused by reaction for the continuity equation of the v th level of the i th species
χ_i	= molar fraction of i th species
χ_{iv}	= molar fraction of i th species in the v th vibrational level

Introduction

LARGE interest is presently devoted to the development of sophisticated codes describing the fluid dynamics and the kinetic

ics of air under different nonequilibrium conditions. In general, the efforts have been concentrated on the fluid dynamic aspects of the problem, whereas the chemical kinetics has been considered a solved problem. In this connection large use has been made of Park's models or with other models essentially based on Park's approach.¹ Basically, Park's models are combustionlike models, with the rates of the elementary processes essentially described by Arrhenius-type equations. Some nonequilibrium effects are considered in these models, namely, the possibility of defining effective temperatures in a multi-temperature approach. This approach, however, can completely hide the nonequilibrium character of the vibrational distributions present in high-enthalpy expanding flows. As a consequence, the rates of elementary processes can differ by orders of magnitude with strong consequences on the final results.

An alternative approach to the problem is to consider a state-to-state approach.^{2,3} Of course, this approach is time consuming and can become prohibitive for realistic two- and three-dimensional codes. However, the state-to-state kinetics can be easily implemented in one-dimensional codes: the results obtained can therefore be used to understand the limitations introduced in the macroscopic treatment of kinetics as usually done in flow solvers.

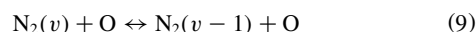
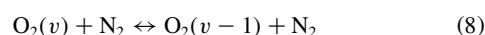
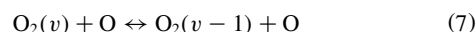
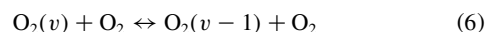
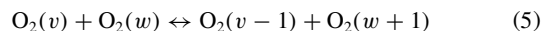
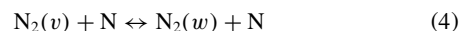
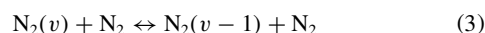
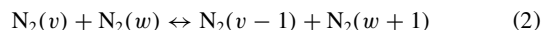
In a previous paper we considered the nonequilibrium vibrational kinetics in the boundary layer of a body traveling at hypersonic flow.⁴ In the present paper we consider the expansion of high-enthalpy flows through a nozzle. In both cases the nonequilibrium character of vibrational distributions is caused by the atom recombination that introduces vibrational quanta on top of the vibrational ladder followed by the spread of vibrational quanta by vibration-vibration (VV) and vibration-translation energy-exchange processes. The resulting nonequilibrium vibrational distributions are such to dramatically enhance the rate of production of NO through the reaction



In particular, a non-Arrhenius behavior of the forward reaction rate can develop, following the strong non-Boltzmann character of the vibrational distributions of $\text{N}_2(v)$. This behavior can strongly modify the NO profile either along the coordinate perpendicular to a body flying at hypersonic velocity⁴ or along the x coordinate in the nozzle expansion.

Method of Calculation

The vibrational kinetics of air mixtures includes the following processes:



Presented as Paper 98-2951 at the AIAA/ASME 7th Joint Thermophysics and Heat Transfer Conference, Albuquerque, NM, 15–18 June 1998; received 28 October 1998; revision received 12 January 1999; accepted for publication 23 February 1999. Copyright © 1999 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved.

*Researcher, Centro di Studio per la Chimica dei Plasmi, Member AIAA.

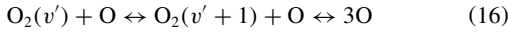
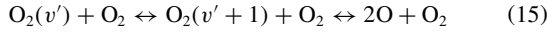
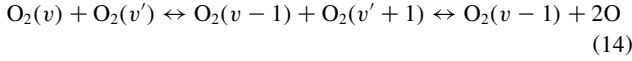
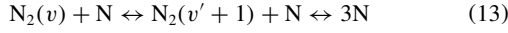
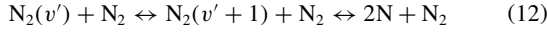
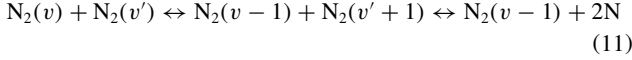
[†]Researcher, Centro di Studio per la Chimica dei Plasmi.

[‡]Full Professor of Chemistry, Dipartimento di Chimica, Università di Bari and Centro di Studio per la Chimica dei Plasmi. Member AIAA.

[§]Research Engineer, Aerothermophysics Section. Member AIAA.

Basically, we solve the vibrational kinetics of N_2 and O_2 coupled to each other through reactions (8–10). Note also that reaction (10) is the only channel for the formation and depletion of NO.

Concerning the dissociation-recombination reactions for N_2 and O_2 , we consider a pseudolevel ($v' + 1$) located just above the last bound level of the diatom (v') through which passes the dissociation-recombination reaction; i.e., we consider the following elementary processes⁴:



In the zero-dimensional kinetics we write a set of coupled first-order differential equations giving the temporal evolution of each vibrational level in the presence of the elementary processes just reported. In this approach the density of the atomic species is seen as two times the concentration of the corresponding pseudolevel. Note also that for NO we consider only the ground vibrational level.

Rate coefficients of the different processes have been discussed in our previous works.^{2–4} A large effort on state-selected NO formation rates has been done by Bose and Candler.⁵

The complexity of air vibrational kinetics makes a realistic fluid dynamic model of the nozzle flow hard to be used. For this reason we have resorted to a simple one-dimensional nozzle flow described by Vincenti and Kruger.⁶ In this case we can write the Euler equation in the following form:

$$\frac{d\rho u A}{dx} = 0, \quad \frac{dp}{dx} + \rho u \frac{du}{dx} = 0, \quad u \frac{du}{dx} + \frac{dh_T}{dx} + \frac{dh_v}{dx} = 0 \quad (17)$$

This equation set should be closed with the ideal gas state equation

$$P = \rho R^* T \quad (18)$$

and the expression for the translational-rotational enthalpy,

$$h_T = \left(\sum_i \chi_i \alpha_i \right) R^* T = \alpha R^* T \quad (19)$$

where $\alpha_i = \frac{5}{2}$ for atomic species and $\alpha_i = \frac{7}{2}$ for the molecular species, and the internal (vibrational and formation) enthalpy

$$h_v = \frac{1}{m} \sum_{i,v} \chi_{iv} (\varepsilon_{iv} + h_i) \quad (20)$$

Such an equation set is still not closed because the χ_{iv} are not determined. The system is completed by the continuity equations for each level of all species to model a state-to-state kinetics:

$$\frac{d\rho_{iv} u A}{dx} = A \dot{\rho}_{iv} \quad (21)$$

where the $\dot{\rho}_{iv}$ have the same expression as in Ref. 7.

The Euler equations have been manipulated to give the following equation for the flow speed:

$$\frac{du}{u dx} = \left[\frac{dA}{A dx} - \frac{dR^*}{R^* dx} + \frac{\gamma}{\alpha} \left(\frac{d\alpha R^*}{\gamma R^* dx} + \frac{dh_v}{c_s^2 dx} \right) \right] / (M^2 - 1) \quad (22)$$

that has been discretized by finite differences and integrated by the implicit Euler with a step-adaptive method described in Ref. 8. Mass

density and gas temperature are calculated algebraically by using the mass and energy continuity equations just listed. The mass fractions c_{iv} are calculated at the same time with the speed equation by solving the finite difference problems coming from

$$\frac{dc_{iv}}{dx} = \frac{\dot{\rho}_{iv}}{u\rho} \quad (23)$$

with the same algorithm used for the flow-speed equation.

The numerical procedure consists in starting from the reservoir at temperature T_0 and at pressure P_0 , and the gas composition is considered in thermodynamical equilibrium. The vibrational distributions in the reservoir are Boltzmann with vibrational temperature equal to the gas temperature. The initial flow velocity is not determined because the transition to supersonic flow happens only for a determined velocity, when the numerator and the denominator become zero at the same time. The initial speed is then obtained by calculating the profile from the reservoir to the throat for different initial speeds until the transition to supersonic flow happens. Once the initial speed and the corresponding inlet flow quantities have been determined, the calculation is continued in the nozzle outlet.

Results and Discussion

The calculations have been performed for a 1-m-long parabolic nozzle having cylindrical symmetry and the axis radius dependence:

$$r(x) = 3.5x^2 - 3.5x + 1 \quad (24)$$

with x expressed in meters ($x_{\text{throat}} = 0.5$ m). The reservoir pressure P_0 is around one bar, and the reservoir temperature T_0 ranges from 4000 to 8000 K. (The subscript 0 will refer to reservoir conditions.)

In Figs. 1a and 1b we have reported the ratio of oxygen (Fig. 1a) and nitrogen (Fig. 1b) first-level temperatures and translational

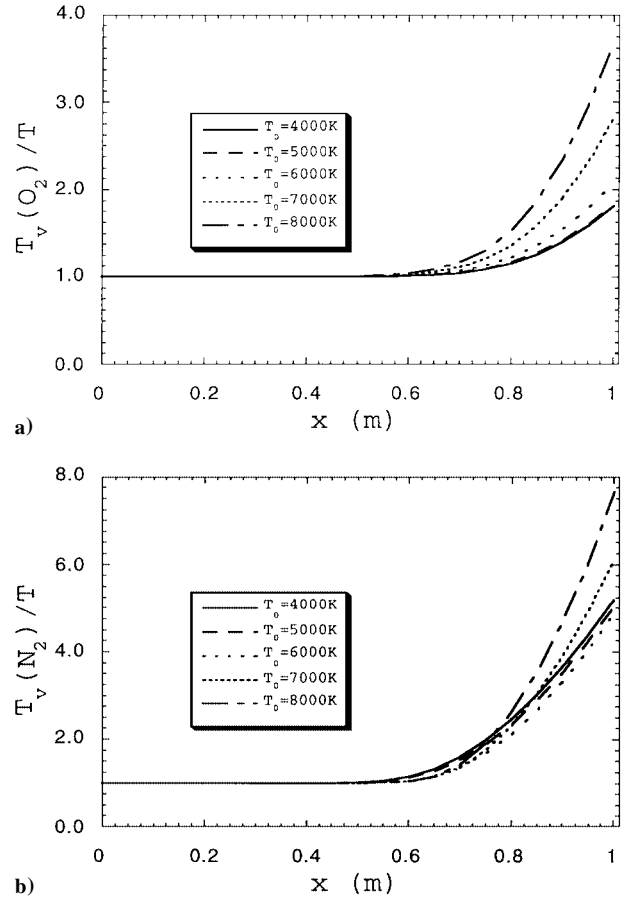


Fig. 1 Ratio between a) O_2 and b) N_2 vibrational temperature T_v and translational temperature T as a function of the nozzle position for different reservoir temperatures.

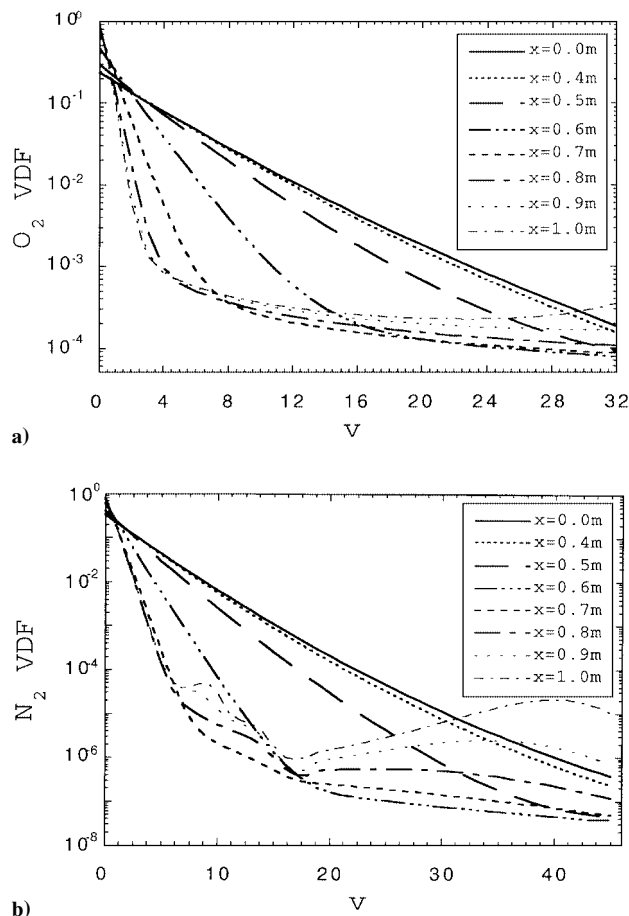


Fig. 2 Vibrational distribution functions (VDFs) for different nozzle positions ($T_0 = 8000$ K).

temperatures. From these figures we can see that the first-level temperature of N_2 is substantially higher than the O_2 first-level temperature as a result of the lower deactivation rates present in the nitrogen system. This result, although important, does not give a realistic view of the nonequilibrium behavior of the vibrational distributions. This point can be understood by looking to the corresponding vibrational distributions for different reservoir temperature and pressure values T_0 , P_0 (see Ref. 9). A sample of the results is reported in Figs. 2a and 2b. The vibrational distributions are very far from a Boltzmann shape, for both O_2 and N_2 , showing a plateau and very complex structures, thus emphasizing the erroneous conclusion about Boltzmann distributions at the local vibrational temperatures. Recall that the form of the calculated vibrational distributions is mainly controlled by the recombination process for both N_2 and O_2 and by the energy exchange processes including the formation of NO from reaction (1).

The nonequilibrium effects manifest themselves at longer distances in the nozzle when the gas temperature cools down, thus favoring the recombination process. At the same time the differences between the vibrational temperatures and the translational one increase with increasing the distance, thus favoring nonequilibrium effects caused by the VV up-pumping mechanism. Note also that the strong nonequilibrium conditions present in the vibrational distributions do not seem to affect macroscopic quantities such as temperature and pressure profiles.⁹

Let us now consider the profiles of N (Fig. 3a) and of NO (Fig. 3b) concentrations. We see a strong correlation between the two profiles. In particular, in all cases except that at $T_0 = 4000$ K, the N profile remains flat with dramatic consequences on the NO profile, which strongly decreases with the distance. At $T_0 = 4000$ K we observe a flat profile of NO as a consequence of the decreasing profile of N. This behavior can be explained by the reverse reaction

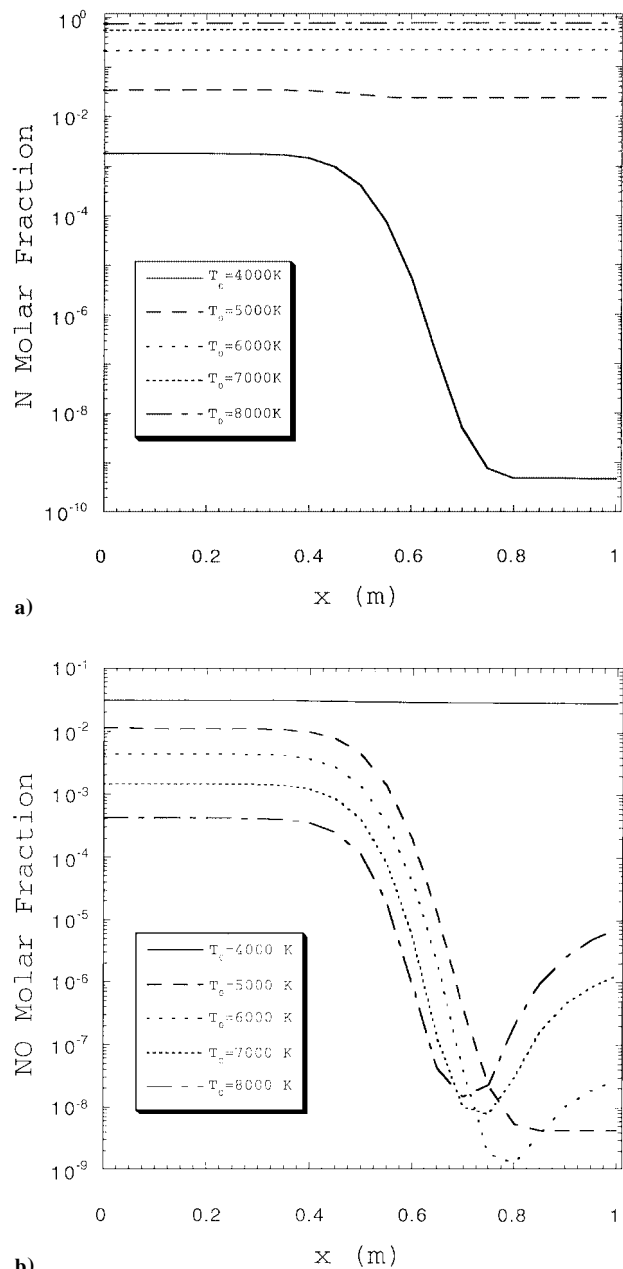
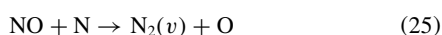


Fig. 3 Molar fraction profiles for different reservoir temperatures.

which practically controls the growth of NO. The NO profile after a given distance, depending on the initial conditions, presents a minimum after which the NO concentration starts growing, which is caused by the strong nonequilibrium character of the NO formation rate as can be appreciated in Fig. 4a. In this figure we have reported the pseudo second-order formation rate of NO through reaction (1) as a function of the inverse of local translational temperature. Axial profiles as a function of $1/T$ have been reported in Fig. 4b. We see that the second-order rate constant follows an Arrhenius-type behavior along the nozzle up to a given $1/T$ value, presenting a non-Arrhenius behavior (negative activation energy) from a given distance on. In particular, a slightly increasing plateau is observed, the magnitude of this plateau depending on the initial conditions. The reported behavior of the rate constant is responsible for the increase of NO concentration from a given distance on. In Fig. 4a we have also reported the experimental rate constant for quasiequilibrium conditions obtained by Monat et al.¹⁰ The satisfactory agreement between calculated and experimental high-temperature results (low $1/T$ values) is an indirect confirmation of the accuracy of the input data used in this work.

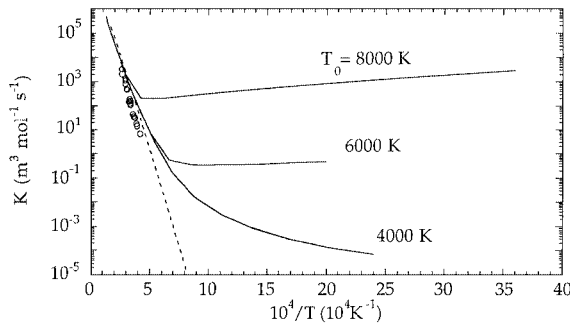


Fig. 4a NO global production rate for the reaction $N_2 + O \leftrightarrow NO + N$ and for different reservoir temperatures T_0 . The symbols are experimental results,¹⁰ and --- is their Arrhenius fit.

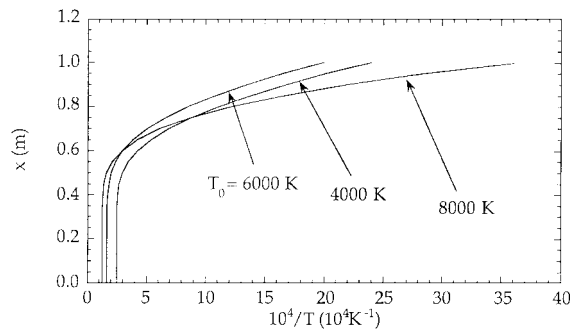


Fig. 4b Nozzle position as a function of the inverse of temperature along the nozzle axis.

Results obtained for nonparabolic nozzles (the so-called F4 nozzle operating at ONERA) closely follow those reported in Figs. 1–4, thus eliminating the uncertainties caused by the use of one-dimensional inviscid flow for parabolic nozzles.⁹

Conclusions

The results presented in this work have shown the role of nonequilibrium vibrational kinetics in the nozzle flow. In particular, the proposed model shows a strong non-Arrhenius character of the formation rate of NO through the reaction of vibrationally excited molecules and oxygen atoms. This behavior is mainly caused by the recombination of N atoms that form strong nonequilibrium vibrational distributions.

The present results, even though qualitative, represent a new attempt to describe nonequilibrium effects in nozzle expansion flows. Future work in this direction should be directed toward a better characterization of input data as well as to dedicated experiments able to monitor the concentration profiles of the different species as well as the vibrational distributions of diatomic molecules along the nozzle axis. Inclusion of these kinetics in two-dimensional nozzle flows should also improve the present treatment.

Acknowledgment

This Note has been partially supported by Agenzia Spaziale Italiana.

References

- ¹Park, C., *Non-Equilibrium Hypersonic Aerothermodynamics*, Wiley, New York, 1990, pp. 326, 327.
- ²Armenise, I., Capitelli, M., Colonna, G., and Gorse, C., "Nonequilibrium Vibrational Kinetics in the Boundary Layer of Re-entering Bodies," *Journal of Thermophysics and Heat Transfer*, Vol. 10, No. 3, 1996, pp. 397–405.
- ³Colonna, G., and Capitelli, M., "Electron and Vibrational Kinetics in the Boundary Layer of Hypersonic Flow," *Journal of Thermophysics and Heat Transfer*, Vol. 10, No. 3, 1996, pp. 406–412.
- ⁴Capitelli, M., Armenise, I., and Gorse, C., "State-to-State Approach in the Kinetics of Air Components Under Re-Entry Conditions," *Journal of Thermophysics and Heat Transfer*, Vol. 11, No. 4, 1997, pp. 570–578.

⁵Bose, D., and Candler, G. V., "Thermal Rate Constants of the $N_2 + O \rightarrow NO + N$ Reaction Using *Ab Initio* 3A," *Journal of Chemical Physics*, Vol. 104, No. 8, 1996, pp. 2825–2833.

⁶Vincenti, W. G., and Kruger, C. H., Jr., *Introduction to Physical Gas Dynamics*, Wiley, New York, 1965, pp. 245–316.

⁷Giordano, D., Bellucci, V., Colonna, G., Capitelli, M., Armenise, I., and Bruno, C., "Vibrationally Relaxing Flow of N_2 Past an Infinite Cylinder," AIAA Paper 95-2072, June 1995; also *Journal of Thermophysics and Heat Transfer*, Vol. 11, No. 1, 1997, pp. 27–35.

⁸Colonna, G., "Step Adaptive Method for Vibrational Kinetics and Other Initial Value Problems," *Supplemento ai Rendiconti del Circolo Matematico di Palermo, Serie II, No. 57*, 1998, pp. 159–163.

⁹Colonna, G., Tuttafesta, M., Capitelli, M., and Giordano, D., "NO Formation in One-Dimensional Nozzle Air Flow with State-to-State Nonequilibrium Vibrational Kinetics," AIAA Paper 98-2951, June 1998.

¹⁰Monat, J. P., Hanson, R. K., and Kruger, C. H., "Shock Tube Determination of the Rare Coefficient for the Reaction $N_2 + O \rightarrow NO + N$," *Proceedings of 17th Symposium (International) on Combustion*, Combustion Inst., Univ. of Leeds, Leeds, England, UK, 1978, pp. 543–552.

View Factors Between Finite Length Rings on an Interior Cylindrical Shell

C. P. Tso* and S. P. Mahulikar†

Nanyang Technological University,
Singapore 639798, Republic of Singapore

Nomenclature

A	= surface area, m^2
D	= diameter, m
d	= distance, m
F_{i-j}	= view factor of surface j as seen by surface i
L	= length, m
r	= radius, m

Subscripts

b	= bottom surface
n	= neighboring surfaces
s	= shell surface
si	= shell interior surface
sid	= shell interior surface of length d
sn	= one of the neighboring shell surfaces
sTT	= total of two neighboring shell surfaces
TT	= total of two neighboring elements
t	= tube surface
u	= upper surface
1	= element 1
2	= element 2 or surface 2; Fig. 2a

Introduction

THE present work is aimed at analyzing surface radiation heat exchange in annular microchannels bounded by two coaxial heat-generating cylinders, for electronics cooling application. The geometry of coaxial cylinders is common to applications such as aircraft engines, heat exchangers, infrared telescopes, reactors, rockets, and tubular furnaces. The view factor, defined, e.g., by Siegel and Howell,¹ is a key element in the computation of radiant interchange between diffusely emitting surfaces. It is also used in conjunction with diffusion and transport codes to calculate the neutral particles

Received 11 August 1998; revision received 18 November 1998; accepted for publication 10 December 1998. Copyright © 1999 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved.

*Associate Professor, School of Mechanical and Production Engineering, Nanyang Avenue.

†Research Engineer, School of Mechanical and Production Engineering, Nanyang Avenue.