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INFLUENCE OF THE SEPARATION OF ELEMENTS ON THE FLOW FIELD IN HYPERSONIC BOUNDARY LAYERS OF AIR IN LOCAL CHEMICAL EQUILIBRIUM

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Abstract—For laminar hypersonic flow of dissociated air in local chemical equilibrium, the boundary-layer equations are solved numerically. For the calculation of the thermodynamic and transport properties of dissociated air, a five component model consisting of N_2, O_2, NO, N and O is employed. Different simplifications are compared to the full solution, which is obtained, if all transport phenomena in the five component model are considered. The results indicate that in the range of investigation the influence of thermal diffusion and the production of the chemical compound NO with respect to species concentration, temperature and heat transfer are negligible. However the separation of the elements nitrogen and oxygen must be considered.

NOMENCLATURE

A_j,	atomic weight of element j;
C,	$= (\rho\mu)/(\rho\mu)_\infty$;
c_p,	specific heat;
c_i,	mole fraction of species i;
$D_{i,k}$,	coefficient of multicomponent diffusion;
D_i^T,	coefficient of multicomponent thermal diffusion;
f',	dimensionless velocity $\frac{u}{u_\infty}$;
h,	enthalpy;
h_i,	enthalpy of species i;
ΔH_r,	enthalpy of reaction r;
$\mathbf{j}_i, j_{i,y}$,	diffusional flux of species i, diffusional flux of species i normal to the wall;
$j_{j,\eta}$,	transformed component of the flux of element j normal to the wall;
k,	thermal conductivity;
K_r,	equilibrium constant of reaction r;
m_i,	production rate of species i;
M_i,	molecular weight;
M,	molecular weight of mixture;
Ma,	Mach number;
p,	pressure;
Pr,	Prandtl number;
q,	energy flux;
q_y,	energy flux normal to the wall;
$\mathcal{R}$,	universal gas constant;
T,	absolute temperature;
u, v,	x- and y-components of velocity;
W_i,	mass fraction of species i;
$\tilde{W}_j$,	mass fraction of element j.

Greek symbols

θ,	heat-transfer parameter;
ϑ,	dimensionless temperature $\frac{T}{T_\infty}$;
ξ, η,	transformed coordinates;
μ,	viscosity;
μ_{ij},	number of elements j in species i;
ν_i', ν_i'',	stoichiometric coefficients for reactants and products;
ρ,	mass density.

Subscripts

ad,	adiabatic;
i, k,	species i, k;
j,	element j;
r,	reaction r;
∞,	outer edge of boundary layer;
w,	wall.

1. INTRODUCTION

LOCAL chemical equilibrium is the limiting case where diffusion time becomes much larger than the time for chemical reaction. At high temperatures occurring in hypersonic boundary layers dissociated air mainly consists of the components N_2, O_2, N, O and NO. Local chemical equilibrium is reached asymptotically with growing boundary-layer thickness.

Presuming that the fractions of elements nitrogen and oxygen are constant in the boundary layer, the chemical species at local chemical equilibrium are only functions of temperature and pressure [1]. Thus only the momentum and energy equation remain to be solved with the equilibrium relations incorporated. Without this simplification additional balance equations for the element fractions have to be considered, which usually are applied if two different gases mix and react as it is the case with combustion problems, e.g. [2].

It is laborious to consider all transport phenomena in a five component gas mixture. Hence, the effect of certain simplifications on the main flow variables in hypersonic boundary layers was investigated. These simplifications include the omission of the separation of elements due to diffusion and of the production of NO and thermal diffusion.

2. CALCULATION OF CHEMICAL SPECIES IN EQUILIBRIUM FLOW

The balance equations for the mass fractions W_i of K species of a chemically reacting fluid are given by

$$\frac{\mathrm{d}W_i}{\mathrm{d}t} + \operatorname{div}\mathbf{j}_i - m_i = 0, \qquad i = 1, \ldots, K. \tag{2.1}$$

In the general case of nonequilibrium flows, the dependence of the source terms m_i on temperature, pressure, and species concentrations is given by chemical kinetics.

However, equations (2.1) cannot be used for the calculation of species concentrations in the limiting case of chemical equilibrium, because of the undetermined mass rate of formation m_i.

With the condition of conservation of elements

$$\sum_{i=1}^{K} A_j \mu_{ij} m_i / M_i = 0, \qquad j = 1, \ldots, L \tag{2.2}$$

where μ_{ij} is the number of elements with the atomic weight A_j in species i with the molecular weight M_i, the undetermined source terms m_i can be eliminated. Multiplying equations (2.1) by $\mu_{ij} A_j / M_i$ and summing up over all K species yields the balance equations for the fractions of elements $\tilde{W}_j$

$$\frac{\mathrm{d}\tilde{W}_j}{\mathrm{d}t} + A_j \operatorname{div} \sum_{i=1}^{K} \mu_{ij} \mathbf{j}_i / M_i = 0, \qquad j = 1, \ldots, L \tag{2.3}$$

where the element fraction is defined as

$$\tilde{W}_j = A_j \sum_{i=1}^{K} \mu_{ij} W_i / M_i. \tag{2.4}$$

Applied to air, equation (2.3) determines either the fraction of nitrogen or oxygen. The second relation determining the element fractions is

$$\sum_{j=1}^{L} \tilde{W}_j = 1. \tag{2.5}$$

From equation (2.3) it can be seen, that elements may separate due to gradients of species concentration even if there are no gradients of element concentrations as it is the case with air. If a gas mixture consists of L elements and K components then a set of $R = K - L$ equilibrium relations exists supplementing equations (2.3) and (2.5). For the general reaction r

$$\sum_{i=1}^{K} \nu_i' S_i \rightarrow \sum_{i=1}^{K} \nu_i'' S_i \tag{2.6}$$

where S_i is a symbol for species i, and ν_i' and ν_i'' are the stoichiometric coefficients of reactants and products, the following equilibrium relations hold

$$K_r = \rho^{\Delta K} \prod_{i=1}^{K} \frac{W_i^{\nu_i'' - \nu_i'}}{M_i}, \qquad r = 1, \ldots, R, \tag{2.7}$$

with

$$\Delta K = \sum_{i=1}^{K} \nu_i'' - \nu_i'.$$

The equilibrium constants K_r are functions of temperature only if the gas is perfect as it will be assumed.

Equation (2.1) which is not useful for the calculation of chemical species in an equilibrium flow can be used for estimating the production rates of N_2, O_2, N, O and NO having calculated first the species concentrations by means of equations (2.3), (2.5), (2.6), (2.7) and the momentum and energy equation. Production rates in a mixture of atoms and molecules of one single element have been discussed and calculated in [3]. As pointed out above, this is possible with the five component model of air also.

3. BOUNDARY-LAYER EQUATIONS AND TRANSFORMATION

The steady boundary-layer equations for constant pressure are

momentum

$$\rho\left(u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y}\right) = \frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right), \tag{3.1}$$

concentration of elements

$$\rho\left(u\frac{\partial \tilde{W}_j}{\partial x} + v\frac{\partial \tilde{W}_j}{\partial y}\right) = -A_j\frac{\partial}{\partial y}\left(\sum_{i=1}^{K} \mu_{ij} j_{i,y} / M_i\right), \tag{3.2}$$

and energy

$$\rho\left(u\frac{\partial h}{\partial x} + v\frac{\partial h}{\partial y}\right) = \mu\left(\frac{\partial u}{\partial y}\right)^2 + \frac{\partial q_y}{\partial y}, \tag{3.3}$$

where the differential of the enthalpy

$$h = \sum_{i=1}^{K} h_i W_i$$

is

$$\mathrm{d}h = \sum_{i=1}^{K} h_i \,\mathrm{d}W_i + c_p \,\mathrm{d}T$$

with

$$c_p = \sum_{i=1}^{K} W_i \frac{\mathrm{d}h_i}{\mathrm{d}T}. \tag{3.4}$$

The diffusional mass and energy flux normal to the wall are

$$j_{i,y} = -D_i^T \frac{\partial}{\partial y}(\ln T) + \sum_{\substack{k=1 \\ k \neq i}}^{K} \rho \frac{M_i M_k}{M^2} D_{ik} \frac{\partial c_k}{\partial y} \tag{3.5}$$

and

$$q_y = -k\frac{\partial T}{\partial y} + \sum_{i=1}^{K} h_i j_{i,y} - \mathscr{R}T \sum_{i=1}^{K} \frac{D_i^T}{c_i M_i}\frac{\partial c_k}{\partial y}, \tag{3.6}$$

where the last term on the r.h.s. of equation (3.6) may be neglected [1].

The r.h.s. of equation (3.2) with gradients of all K species fractions, can be rearranged such that it includes the gradient of the fraction of a single species, only, and an additional term of thermal diffusion [4] by the aid of the equilibrium relations (2.7) and of van t'Hoff's relation

$$\frac{\partial \ln K_r}{\partial \ln T} = \Delta H_r / \mathscr{R}T. \tag{3.7}$$

A corresponding rearrangement can be performed with the energy equation.

Applying the Howarth-transformation

$$\eta = \frac{u_\infty}{\sqrt{(2\xi)}} \int_0^y \rho \, \mathrm{d}y, \qquad \xi = \int_0^x (\rho\mu)_\infty u_\infty \, \mathrm{d}x \tag{3.8}$$

with the dimensionless variables $f' = u/u_\infty$ and $\vartheta = T/T_\infty$ and with $C = \rho\mu/(\rho\mu)_\infty$ the following ordinary differential equations are derived from (3.1)–(3.3) for boundary conditions which only depend on the transformed coordinate η

$$(Cf'')' + ff'' = 0, \tag{3.9}$$

$$f(\tilde{W}_j)' + A_j\left(\frac{C}{\mu}\sum_{i=1}^{K}\frac{\mu_{ij}}{M_i}\left(D_i^T(\ln\vartheta)' - \sum_{\substack{k=1\\k\neq i}}^{K}\rho\frac{M_i M_k}{M^2}D_{ik}c_k'\right)\right)' = 0, \tag{3.10}$$

$$\frac{c_p}{c_{p\infty}} f\vartheta' + \sum_{i=1}^{K}\frac{h_i}{c_{p\infty}T_\infty} fW_i' - \frac{u_\infty^2}{c_{p\infty}T_\infty}C(f'')^2 - \left(C\left(\frac{c_p\vartheta'}{c_{p\infty}Pr} + \sum_{i=1}^{K}\frac{h_i}{c_{p\infty}T_\infty}\left(\frac{D_i^T}{\mu}(\ln\vartheta)' - \sum_{\substack{k=1\\k\neq i}}^{K}\rho\frac{M_i M_k}{M^2}D_{ik}c_k'\right)\right)\right)' = 0. \tag{3.11}$$

The Prandtl number is $Pr = \dfrac{\mu c_p}{k}$.

The boundary conditions of the velocity field are

$$f_w = f_w' = 0 \quad \text{and} \quad f_\infty' = 1. \tag{3.12}$$

At a wall not permeable to mass, the diffusional flux of elements normal to the wall vanishes. Hence a coupled boundary condition for the equation of element fraction and energy is the following

$$(j_{j,\eta})_w = A_j\frac{C}{\mu}\sum_{i=1}^{K}\frac{\mu_{ij}}{M_i} \times \left(D_i^T(\ln\vartheta)' - \sum_{\substack{k=1\\k\neq i}}^{K}\rho\frac{M_i M_k}{M^2}D_{ik}c_k'\right) = 0. \tag{3.13}$$

The second boundary condition at $\eta = 0$ is given by the constant wall temperature. In the special case of an adiabatic wall where the heat flux is zero, the gradients of temperature and element fractions vanish at the wall. The conditions at the outer edge of the boundary layer are given by the values of the undisturbed flow.

4. CALCULATION PROCEDURE

The coupled equations of momentum, energy and element fraction are solved by a Hermitian type finite difference scheme of high accuracy [5]. Besides the field variables, their first derivatives are unknowns, and therefore can be incorporated explicitly into the difference scheme as boundary conditions. The non-linear terms of the differential equations are treated by an iteration procedure with a high rate of convergence [6]. The iterative calculation procedure is shown in the flow diagram, Fig. 1. The thermodynamic properties and equilibrium constants are approximated by the least squares method according to the data given in [7]. The fractions of species are calculated after the equilibrium constant method, e.g. [8], transport properties as proposed in [9].

5. RESULTS AND DISCUSSION

Flat plate boundary-layer calculations have been performed for flight conditions as recommended at an AGARD-meeting in Teddington, England in 1967, see Table 1. For a wall, not permeable to mass, different thermal boundary conditions have been studied, the adiabatic and cooled wall. The temperatures of the cooled and adiabatic wall, ϑ_w and $\vartheta_{w,\mathrm{ad}}$ define the heat-transfer parameter

$$\theta = (\vartheta_{w,\mathrm{ad}} - \vartheta_w)/(\vartheta_{w,\mathrm{ad}} - 1). \tag{5.1}$$

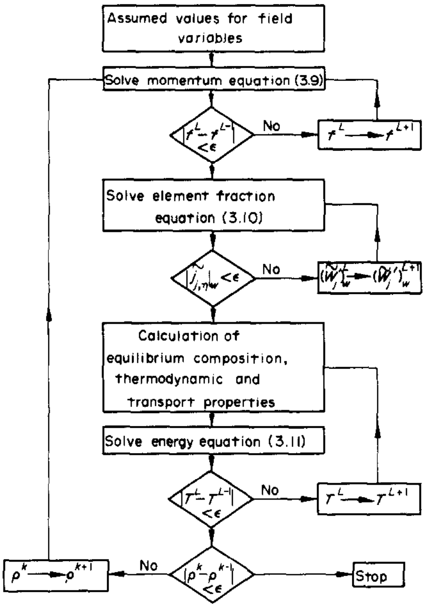


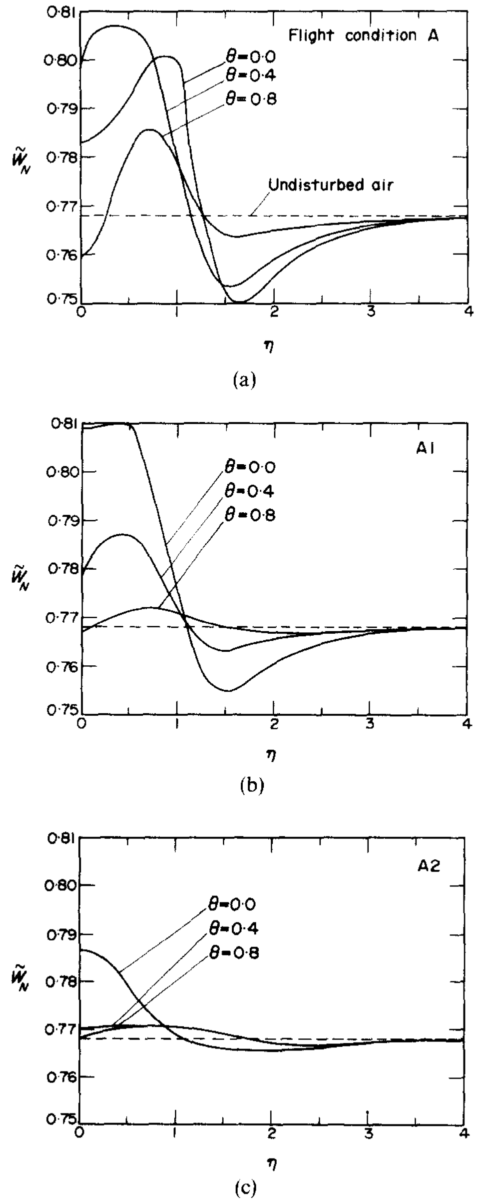
FIG. 1. Flow diagram for solving the boundary layer equations.

Table 1. Flight conditions

		AGARD-A	AGARD-A1	AGARD-A2
H	(km)	30·480	30·48	30·48
u_∞	(km/s)	6·096	4·572	3·048
p_∞	(atm)	1·0997 . 10^{-2}	1·0997 . 10^{-2}	1·0997 . 10^{-2}
T_∞	(°K)	226·98	226·98	226·98
ρ_∞	(g/cm^3)	1·7028 . 10^{-5}	1·7028 . 10^{-5}	1·7028 . 10^{-5}
Ma_∞	—	20·14	15·11	10·07

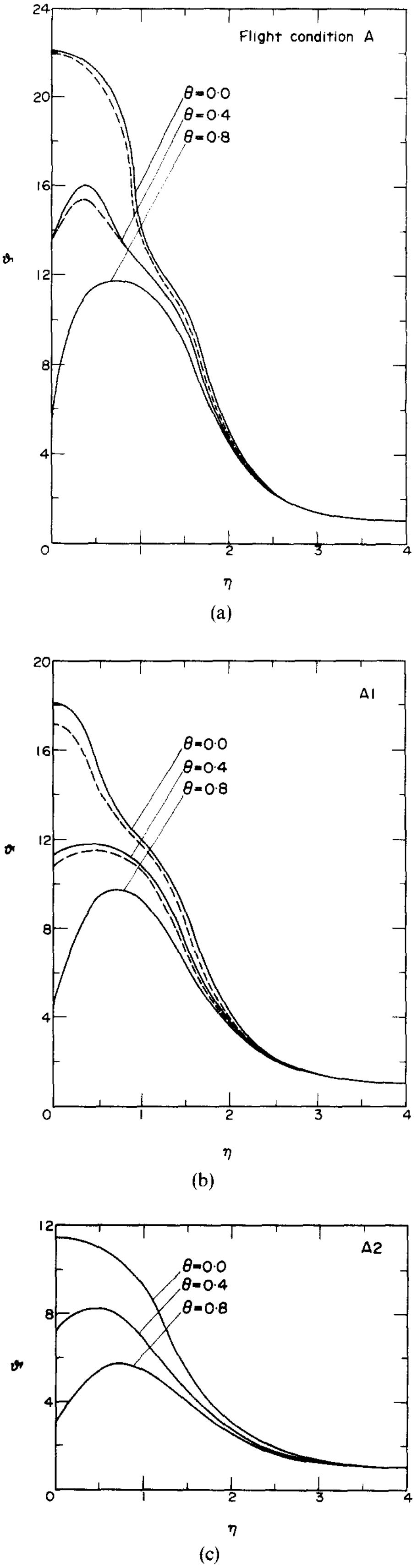
Figures 2(a)–(b) indicate that the element fraction of nitrogen $\tilde{W}_N$ and of oxygen $\tilde{W}_O = 1 - \tilde{W}_N$ are changed accordingly within the boundary layer, compared to undisturbed air. This separation of elements, depending on diffusion of species, is mainly due to the fact that dissociation of molecular oxygen O_2 starts at lower temperatures than that of molecular nitrogen N_2, and that diffusion coefficients of atoms and molecules are remarkably different.

With decreasing Mach number Ma_∞ temperatures decrease as shown in Figs. 3(a)–(c), and so the influence of the separation of elements vanishes at flight condition A2, Fig. 3(c). The neglect of the separation of elements, marked by the dashed line, yields by far, larger errors of the temperature distribution than the neglect of the thermal diffusion and production of NO, which are too small as to be shown in the figures.



(a)
(b)
(c)

FIG. 2(a–c). Distributions of element fraction of nitrogen $\tilde{W}_N$ for various heat-transfer parameters θ.



(a)
(b)
(c)

FIG. 3(a–c). Temperature distributions for various heat-transfer parameters θ. ——, all transport phenomena; – – –, no separation of elements.

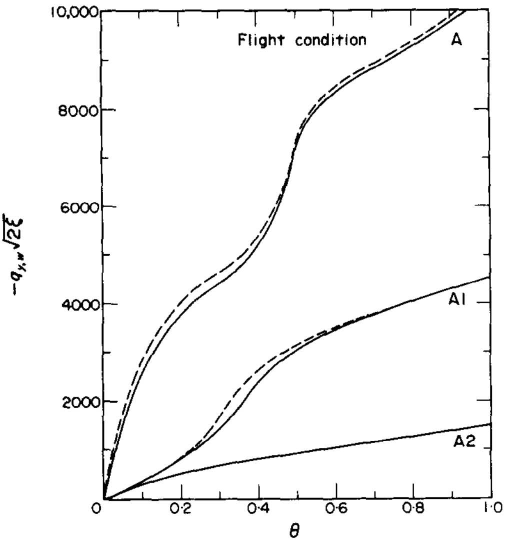


FIG. 4. Heat-transfer rate $q_{y,w}\sqrt{(2\xi)}$ vs heat-transfer parameter θ. ——, all transport phenomena; ---, no separation of elements.

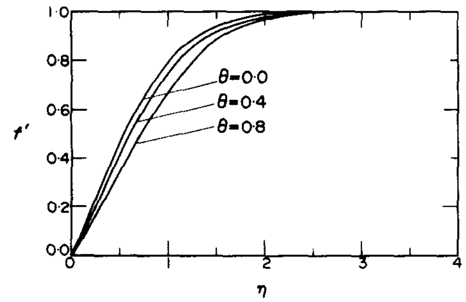


FIG. 5. Velocity distributions for flight condition *A*.

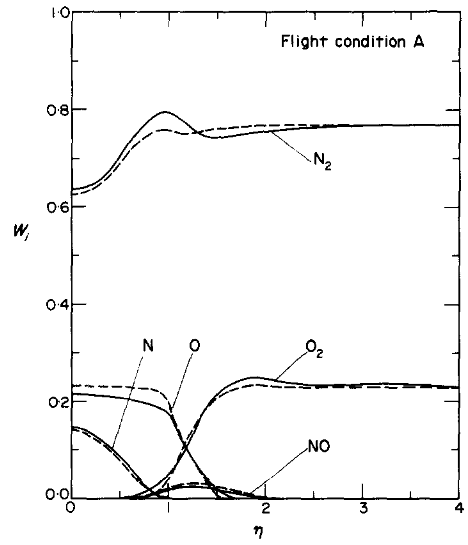


FIG. 6. Distributions of species concentration for adiabetic wall.

From Fig. 4, which demonstrates the dependence of heat-transfer parameter θ on heat transfer rate $q_{y,w}\sqrt{(2\xi)}$, the influence of neglecting the separation of elements again, becomes obvious. There is a remarkable influence neither of thermal diffusion and production of NO nor of the separation of elements on the velocity profile, which for case A is given in Fig. 5. The strong influence of element separation on the concentration profiles of chemical species is following from Fig. 6.

CONCLUSION

In hypersonic boundary layers, dissociated air mainly consists of the five components N_2, O_2, NO, N and O. The influence of thermal diffusion and the production of NO on the flow variables was shown to be negligible. This is demonstrated by a systematic investigation whereby the system was maintained uninfluenced by the production of NO or the thermal diffusion or the separation of elements. Concentration and temperature profiles as well as heat-transfer rates considerably depend on separation of elements, whereas the velocity profile does not. Because of the separation of elements, it is not sufficient to take only into account the balance equations of momentum and energy and the equilibrium relations. Moreover, a balance equation for elements must be considered for boundary layers of dissociated air in local chemical equilibrium.

REFERENCES

1. D. Straub, W. Schönauer, A. Schaber, S. Lin and E. Adams, Stationäre laminare Hyperschallgrenzschichten um ein Rotationshyperboloid bei thermochemischem Gleichgewicht der Luft, DLR FB 72-16 (1972).
2. F. A. Williams, *Combustion Theory*. Addison-Wesley, Reading (1965).
3. M. Jischa, Production terms in chemically reacting equilibrium flows, discussed for a binary mixture laminar boundary layer flow, *Int. J. Heat Mass Transfer* **15**, 2261–2273 (1973).
4. H. Eickhoff and F. Thiele, Entmischung von Stickstoff und Sauerstoff in laminaren Hyperschallgrenzschichten bei lokalem thermochemischen Gleichgewicht der Luft, DLR FB 74-63 (1974).
5. F. Thiele, Differenzenverfahren vom Hermiteschen Typ für gewöhnliche Differentialgleichungen höherer Ordnung, IB 9, Lehrstuhl für Überschalltechnik, TU Berlin (1973).
6. E. Elsholz and W. Haase, Eine Konvergenzbeschleunigung für Fixpunktgleichungen, IB 5, Lehrstuhl für Überschalltechnik, TU Berlin (1972).
7. D. R. Stull and M. Prophet, Janaf Thermochemical Tables, NSRDS-NBS 37 (1971).
8. F. J. Zeleznik and S. Gordon, Calculation of complex chemical equilibria, *Ind. Engng Chem.* **60**, 27–57 (1968).
9. D. Straub, Exakte Gleichungen für die Transportkoeffizienten eines Fünf-Komponentengemisches als Modellgas dissoziierter Luft, DLR FB 72-34 (1974).

INFLUENCE DE LA SEPARATION DES ELEMENTS SUR LE CHAMP DES VITESSES DANS LES COUCHES LIMITES HYPERSONIQUES D'AIR EN EQUILIBRE CHIMIQUE LOCAL

Résumé—Les équations de la couche limite sont résolues numériquement dans un écoulement laminaire d'air dissocié en équilibre chimique local. Un modèle à cinq composants comprenent N_2, O_2, NO, N et O est utilisé pour calculer les propriétés thermodynamiques et les propriétés de transport de l'air dissocié. Diverses simplifications sont comparées à la solution complète qui est obtenue en considérant l'ensemble des phénomènes de transport dans le modèle à cinq composantes. Les résultats montrent que l'influence de la diffusion thermique et de la production du composé chimique NO sur la concentration des espèces chimiques, la température et le transfert thermique est négligeable dans le domaine étudié. Cependant la séparation des éléments oxygène et azote doit être considérée.

DER EINFLUSS DER TRENNUNG DER ELEMENTE AUF DAS STRÖMUNGSFELD IN HYPERSCHALL-GRENZSCHICHTEN VON LUFT IM CHEMISCHEN GLEICHGEWICHT

Zusammenfassung—Für laminare Hyperschallströmung dissoziierter Luft im lokalen chemischen Gleichgewicht werden die Grenzschichtgleichungen numerisch gelöst. Zur Berechnung der Stoff- und Transportgrößen dissoziierter Luft wird ein Modell der Luft, bestehend aus den Komponenten N_2, O_2, NO, N und O verwendet. Unterschiedliche Vereinfachungen werden mit der vollständigen Lösung verglichen, die sich unter Berücksichtigung aller Transportvorgänge in dem Fünfkomponentengemisch ergibt. Die Ergebnisse zeigen, daß die Thermodiffusion und die Bildung der chemischen Komponente NO in dem untersuchten Bereich vernachlässigt werden können, daß aber die Trennung der Elemente Sauerstoff und Stickstoff infolge Diffusion berücksichtigt werden muß.

ВЛИЯНИЕ РАЗДЕЛЕНИЯ ЭЛЕМЕНТОВ НА ПАРАМЕТРЫ ПОТОКА В ГИПЕРЗВУКОВЫХ ПОГРАНИЧНЫХ СЛОЯХ ВОЗДУХА ПРИ ЛОКАЛЬНОМ ХИМИЧЕСКОМ РАВНОВЕСИИ

Аннотация — Решаются численно уравнения пограничного слоя для ламинарного гиперзвукового потока диссоциированного воздуха при локальном химическом равновесии. Для расчета гидродинамических характеристик и параметров переноса диссоциированного воздуха, используется пятикомпонентная система, состоящая из N_2, O_2, $И_0$, N и O. Различные упрощения сравниваются с полным решением, полученным при условии, что в этой пятикомпонентной системе рассматриваются все явления переноса. Результаты показывают, что в диапазоне исследования можно пренебречь влиянием термодиффузии и образованием продуктов химического соединения N_0 на концентрацию смеси, температуру и теплоперенос. Однако следует учитывать разделение элементов азота и кислоргда.