

8. S. Perez, H. Schmiedel, and B. Schramm, "Second interaction virial coefficients of the noble gas-hydrogen mixtures," *Z. Phys. Chem.*, 123, No. 1, 35-38 (1980).
9. B. Schramm, E. Elias, and R. Pilger, "Second interaction virial coefficients of argon-hydrogen mixtures," *Chem. Phys. Letters*, 88, No. 5, 549-552 (1982).
10. E. W. Crain and R. E. Sontag, "The P-V-T behavior of nitrogen, argon, and their mixtures," *Adv. Cryogenic Eng.*, 11, 379-391 (1966).
11. V. V. Altunin, O. D. Koposhilov, and E. N. Sychev, "Investigation of volume and pressure effects of mixing in dense gas solutions. Helium-carbon dioxide system," *Trudy Mosk. Energ. Inst.*, No. 234, 22-30 (1975).
12. E. Naumowicz, K. Olesiak, and W. Woycicki, "Excess enthalpy of argon-helium mixtures," *J. Chem. Thermodynamics*, 13, No. 9, 899-900 (1981).
13. V. V. Altunin, D. O. Kuznetsov, and V. F. Bondarenko, "Experimental investigation of the thermodynamic properties of binary gas mixtures. Enthalpy, isobaric specific heat," *Teplofiz. Vys. Temp.*, 12, No. 3, 513-518 (1974).

CALCULATION OF THE TRANSPORT COEFFICIENTS IN MULTICOMPONENT GAS MIXTURES

I. V. Lebedev and V. V. Ryabov

UDC 517.9:533.7

An approximate method is discussed for calculating the transport coefficients in multicomponent gas mixtures.

It is well known that the numerical integration of the equations of gasdynamics for multicomponent mixture with transport coefficients calculated rigorously using kinetic theory is beset with serious difficulties. This is because 1) the mass diffusion flux of the i -th component and the heat flux depend on the fluxes of all the other components and their gradients; 2) for an N -component mixture it is necessary to compute the set of Ω_{ij} integrals, where $i, j = 1, \dots, N$; 3) in order to calculate the transport coefficients ratios of determinants of orders N and $N + 1$ are required. Hence with increase in the number of components, the number of computational operations and the memory required progressively increase.

These difficulties have stimulated the development of various approximate methods of calculating transport coefficients. A widely used approximate relation for the thermal conductivity and viscosity is based on the fact that the nondiagonal elements in the determinants are much smaller than the diagonal elements, and thus perturbation theory can be used. It should be noted that satisfactory results from first- and second-order perturbation theory can be achieved only by introducing an additional empirical parameter fitted to experimental data [1].

In the simplest method of calculating the mass-exchange coefficients, the diffusion coefficients are set equal to each other and the coefficient of thermal diffusion is ignored even where this leads to serious error.

The bifurcation method [2, 3] is used widely in engineering calculations. The use of different diffusion coefficients for the different components leads to only a slight complication of the algebra and a somewhat increased execution time for the calculations. The main advantage of this method is that the resulting expression for the mass diffusion flux of the i -th component involves only variables and their gradients characterizing the system as a whole and the i -th component, but not any of the other components. In addition, in the calculation of the mass diffusion flux, it is sufficient to use only N quantities dependent on the molecular properties of the components. The error in the coefficients can be as large as 10% for the systems studied in [2].

In the approximation method used in [4], the mass diffusion flux of the i -th component is directly proportional to the concentration gradient of the i -th component only. In [4], approximate expressions were given for the constants of proportionality between these quantities (the effective diffusion coefficients) and it was shown that in several cases involv-

Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 48, No. 2, pp. 267-272, February, 1984. Original article submitted October 5, 1983.

ing boundary layers, they could be approximated accurately by functions only of the binary diffusion constants and the values of the concentration on the wall and on the outer edge of the boundary layer.

We present an approximation method for the transport coefficients of a multicomponent gas mixture based on isolating the dominant term in a double polynomial expansion of the correction to the first-order Chapman-Enskog theory. Quantities calculated with the approximate relations for the thermal conductivity, viscosity, and diffusion coefficients obtained here are compared with those calculated using the standard methods.

In order to obtain a closed system of gasdynamic equations for a mixture of N nonreacting gases in the absence of external forces, the diffusion velocity of the i -th component V_i^1 , the stress tensor P_{rk} , and heat flux q must be expressed in terms of the hydrodynamic quantities: u , the average velocity of the mixture; T , the temperature of the mixture; and n_j ($j = 1, \dots, N$), the concentrations of the components. The solution of this problem in the hydrodynamic approximation has been worked out using the Chapman-Enskog method [1].

We will look for a solution of the system of kinetic equations for the distribution function of each component in the mixture in the form of an asymptotic series in a small parameter (we choose the Knudsen number). Using for the zeroth approximation a local Maxwellian distribution function f_i^0 , we obtain for the first-order correction $\varphi_i^{(1)}$ [1]:

$$f_i^{(0)} \left[\left(\frac{m_i c^2}{2kT} - \frac{5}{2} \right) c_r^i \frac{\partial \ln kT}{\partial x_r} + \frac{m_i}{kT} \left(c_r^i c_l^i - \frac{1}{3} c^2 \delta_{rl} \right) \frac{\partial u_r}{\partial x_l} + \frac{n}{n_i} c_r^i d_r^i \right] = - \sum_{j=1}^N n_i n_j I_{ij} [\varphi^{(1)}], \quad (1)$$

where c^i and m_i are respectively the velocity and particle mass of the i -th component, $n = \sum_{i=1}^N n_i$, k is the Boltzmann constant, δ_{rl} is the Kronecker delta, and the integrals $I_{ij}[\varphi^{(1)}]$ are given in [1].

The set of thermodynamic diffusion forces $d_r^i = \frac{\partial}{\partial x_r} \left(\frac{n_i}{n} \right) + \left(\frac{n_i}{n} - \frac{m_i n_i}{\bar{m} n} \right) \frac{\partial \ln p}{\partial x_r}$, where

$\bar{m} = \sum_{i=1}^N m_i n_i / n$, $p = nkT$, are not linearly independent since $\sum_{i=1}^N d_r^i = 0$. In analogy with [5], we transform the set of vectors d^i ($i = 1, \dots, N$) to the set $D^{(p)}$ ($p = 0, 1, \dots, N-1$):

$$\frac{n}{n_i} d_r^i = \sum_{p=0}^{N-1} \frac{m_i}{\bar{m}} P_i^{(p)} D_r^{(p)}. \quad (2)$$

In (2) we use for the matrix elements of the linear transformation the Waldman-Trubnicher polynomials $P_i^{(p)} = \sum_{k=0}^p \alpha_k m_i^k$, which satisfy the following recurrence relations [5]:

$$P_i^{(0)} = 1, \quad P_i^{(1)} = (m_i - \langle m \rangle) / (\langle m^2 \rangle - \langle m \rangle^2),$$

$$\langle m^k \rangle = \sum_{i=1}^N m_i^{k+1} n_i / \bar{m} n.$$

Since $\sum_{i=1}^N d^i = 0$, we have $D^{(0)} = 0$, and the other $N-1$ vectors $D^{(p)}$ ($p = 1, \dots, N-1$) are linearly independent.

Following [1], we seek the general solution of (1) as the sum of a particular solution and the general solution of the homogeneous integral equation. The $N + 4$ arbitrary constants in the general solution are chosen so that $\varphi_i^{(1)}$ does not contribute to n_i , u , T . The general solution of (1), using (2), can then be written in the form

$$\varphi_i^{(1)} = -\frac{1}{n} A^i \frac{m^i}{m} c_r^i \frac{\partial \ln kT}{\partial x_r} - \frac{1}{n} \frac{m^i}{m} B^i \left(c_r^i c_l^i - \frac{1}{3} c^{i2} \delta_{rl} \right) \frac{\partial u_l}{\partial x_r} + \sum_{p=1}^{N-1} A^{i(p)} \frac{m_i}{m} c_r^i D_r^{(p)}. \quad (3)$$

Integral equations for the functions $A^{i(p)}$, A^i , and B^i , satisfying the condition that $\varphi_i^{(1)}$ does not contribute to n_i , u , and T , are obtained by substituting (3) into (1) and equating the coefficients of the gradients of like quantities:

$$-f_i^{(0)} m_i c_r^i P_i^{(p)} = \sum_{j=1}^N n_i n_j I_{ij} [m c_r A^{(p)}], \quad p = 1, \dots, N-1, \quad (4)$$

$$f_i^{(0)} \left(\frac{m_i c^{i2}}{2kT} - \frac{5}{2} \right) c_r^i = \sum_{j=1}^N \frac{n_i n_j}{nm} I_{ij} [m c_r A],$$

$$f_i^{(0)} \frac{m_i}{kT} \left(c_r^i c_l^i - \frac{1}{3} c^{i2} \delta_{rl} \right) = \sum_{j=1}^N \frac{n_i n_j}{nm} I_{ij} \left[m \left(c_r c_l - \frac{1}{3} c^2 \delta_{rl} \right) B \right].$$

Following [5], we look for solutions of the integral equations in the form of double polynomial expansions:

$$A^{i(p)} = \sum_{s=0}^{N-1} \sum_{q=0}^{\infty} a_{sq}^{(p)} P_i^{(s)} S_{(3/2)i}^{(q)}, \quad p = 1, \dots, N-1, \quad (5)$$

$$L^i = \sum_{s=0}^{N-1} \sum_{q=0}^{\infty} l_{sq} \Pi_i^s S_{(j)i}^{(q)}.$$

In (5) L^i stands for A^i and B^i , l_{sq} for a_{sq} and b_{sq} , and $j = 3/2$ and $5/2$. The $S_{(j)i}^{(q)}$ are the Sonine polynomials and $\Pi_i^{(s)} = \sum_{k=0}^s \beta_k m_i^k$ are the Waldman-Trubenchbacher polynomials, which satisfy

the recurrence relations [5]: $\Pi_i^{(0)} = 1$, $\Pi_i^{(1)} = (m_i - \bar{m})/(\bar{m}^2 - \bar{m}^2)$, $\bar{m}^k = \sum_{i=1}^N m_i^k n_i/n$.

The series for $A^{i(p)}$, A^i , and B^i are replaced by their first nonvanishing terms $a_{p0}^{(p)}$, a_{01} , and b_{00} , respectively. We multiply (4) by $P_i^{(p)}$, $S_{(3/2)i}^{(1)}$, and 1, respectively, and integrate with respect to velocity and sum over components. We note that the above terms are the only ones in (5) which these operations leave nonvanishing. In addition, the term $a_{01} S_{(3/2)i}^{(1)}$ is the only one in the expansion (5) that contributes to the thermal conductivity. Similarly only the terms $a_{p0}^{(p)} P_i^{(p)}$ ($p = 1, \dots, N-1$) and b_{00} contribute to the diffusion coefficients and viscosity, respectively. We refer to terms with $a_{p0}^{(p)}$, a_{01} , and b_{00} as dominating in (5) and we use variational methods to find them. Note that the dominant terms can always be separated out from the solution in the form (3) and (5). We obtain the results:

$$a_{p0}^{(p)} = \frac{3\bar{m}}{8nR^{(p)}}, \quad p = 1, \dots, N-1, \quad (6)$$

$$b_{00} = \frac{5\bar{m}}{16kTG}, \quad a_{01} = -\frac{15\bar{m}}{16R}.$$

The coefficients in relations (5) are functions of the Ω_{ij} integrals given in [1]:

$$R = \sum_{i,j=1}^N \frac{n_i n_j}{n^2} \frac{m_i m_j}{(m_i + m_j)^3} \left[\frac{55}{2} (m_i^2 - m_i m_j) \Omega_{ij}^{(1,1)} - 10 (m_i^2 - m_i m_j) \Omega_{ij}^{(1,2)} + 2 (m_i^2 - m_i m_j) \Omega_{ij}^{(1,3)} + 8 m_i m_j \Omega_{ij}^{(2,2)} \right], \quad (7)$$

$$G = \sum_{i,j=1}^N \frac{n_i n_j}{n^2} \frac{m_j}{(m_i + m_j)} \Omega_{ij}^{(2,2)},$$

$$R^{(p)} = \sum_{i,j=1}^N \frac{n_i n_j}{n^2} \frac{m_i m_j}{(m_i + m_j)} (P_i^{(p)} - P_j^{(p)})^2 \Omega_{ij}^{(1,1)}.$$

The calculated values of the coefficients $A^{i(p)}$, A^i , and B^i are used to get the quantities V^i , q , and p_{rs} :

$$\begin{aligned} V_r^i &= - \sum_{p=1}^{N-1} \sum_{l=0}^p \frac{3kT}{8n} \frac{P_i^{(p)}}{R^{(p)}} \left[\alpha_l \frac{\partial \bar{m}^l}{\partial x_r} + (\bar{m}^l - \langle m^l \rangle) \frac{\partial \ln p}{\partial x_r} \right], \\ p_{rs} &= - \frac{5}{16} \frac{kT}{G} \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \delta_{rs} \frac{\partial u_l}{\partial x_l} \right), \\ q &= - \frac{75}{32} \frac{kT}{R} \frac{\partial kT}{\partial x_r} - \frac{15}{16} (kT)^2 \sum_{p=1}^{N-1} \sum_{k,l=0}^p \frac{\alpha_l \bar{m}^l}{R^{(p)}} \left[\alpha_k \frac{\partial \bar{m}^k}{\partial x_r} + (\bar{m}^k - \langle m^k \rangle) \frac{\partial \ln p}{\partial x_r} \right]. \end{aligned} \quad (8)$$

And the system of gasdynamic equations is now closed.

Using the usual expressions for the quantities given in (8)

$$\begin{aligned} V_r^i &= - \sum_{j=1}^N D_{ij} d_r^j - D_i^T \frac{\partial}{\partial x_r} (\ln kT), \\ q_r &= - \lambda' \frac{\partial T}{\partial x_r} - p \sum_{i=1}^N D_i^T d_r^i + \frac{5}{2} kT \sum_{i=1}^N n_i V_r^i, \\ p_{rs} &= - \eta \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \delta_{rs} \frac{\partial u_l}{\partial x_l} \right), \end{aligned}$$

we obtain the diffusion coefficients D_{ij} , the thermodiffusion coefficient D_i^T , the thermal conductivity λ' , and the viscosity η :

$$\begin{aligned} D_{ij} &= \frac{3kT}{8n} \sum_{p=1}^{N-1} \frac{P_i^{(p)} P_j^{(p)}}{R^{(p)}}, \quad D_i^T = 0, \\ \lambda' &= \frac{75}{32} \frac{k^2 T}{R}, \quad \eta = \frac{5}{16} \frac{kT}{G}. \end{aligned} \quad (9)$$

Note that in (5) if we use only the dominant terms, then $D_i^T = 0$. Hence, a nonzero thermodiffusion coefficient in expansion (5) can only be obtained if we take into account additional "interference" terms.

Use of the transformation (2) allowed us to express V^i and q in terms of the gradients of average quantities only: p , T , \bar{m}^k , $k = 1, \dots, N-1$, where the coefficients of these gradients depended only on quantities characterizing the i -th component and the system as a whole. As was shown in [2], these properties of (8) simplify considerably the numerical integration of the system of gasdynamic equations. Also the transport coefficients (9) are given in compact analytical form, and it is not required to calculate the ratio of determinants of orders $N+1$ and N . However, unlike the bifurcation approximation, in the calcu-

lation of the kinetic coefficients (9), as in the calculation of the transport coefficients using traditional kinetic theory, one must use the entire set of Ω_{ij} integrals.

To test the accuracy of (9), the results using these relations were compared to those calculated in [6] using traditional formulas obtained with the Chapman-Enskog method. The diffusion coefficients were compared for the three-component systems N_2-O_2-NO and $N-O-NO$, and the viscosity and thermodiffusion coefficients were compared for the same three-component systems and the five-component system $N_2-O_2-NO-N-O$ for different concentrations. It was found that the errors in the diffusion coefficients did not exceed 3%, except for the diffusion coefficients with NO as one of the components, where the error was as large as 9%. The error in the viscosities did not exceed 2.5%, and the error in the thermodiffusion coefficients was less than 6%. We note that in a two-component system ($N = 2$), D_{ij} given by (9) agrees with the result obtained using the Chapman-Enskog method [1].

Attempts to separate out one or several dominant "interference" terms in expansion (3), which would give a nonzero value for the thermodiffusion coefficient, were not successful.

LITERATURE CITED

1. J. Ferziger and G. Kaper, *Mathematical Theory of Transport Processes in Gases* [Russian translation], Mir, Moscow (1976).
2. R. M. Kendall, R. A. Rindall, and E. P. Barlett, "A multicomponent boundary layer chemically coupled to an ablating surface," *AIAA J.*, No. 6, 9-19 (1967).
3. V. V. Ryabov, "Approximation method of calculating the transport coefficients in a multicomponent mixture," *Inzh.-Fiz. Zh.*, 44, No. 2, 265-272 (1983).
4. G. A. Tirskii, "Calculation of the effective coefficients of diffusion in laminar dissociating multicomponent boundary layers," *Prikl. Mat. Mekh.*, 33, No. 1, 180-192 (1969).
5. V. A. Matsuk and B. A. Rykov, "Extension of the Chapman-Enskog method to mixtures of reacting gases," *Zh. Vychisl. Mat. Mat. Fiz.*, 18, No. 1, 167-182 (1978).
6. V. V. Ryabov, "Calculation of the transport coefficients of equilibrium dissociating air," *Trudy TsAGI*, Issue 2045, 3-14 (1980).