Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications
Supplement I—Transport Properties

Sanford Gordon
Sanford Gordon & Associates
Cleveland, Ohio

and

Bonnie J. McBride and Frank J. Zeleznik.
Lewis Research Center
Cleveland, Ohio

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COMPUTER PROGRAM FOR CALCULATION OF COMPLEX CHEMICAL EQUILIBRIUM COMPOSITIONS AND APPLICATIONS

SUPPLEMENT I - TRANSPORT PROPERTIES

Sanford Gordon
Sanford Gordon & Associates
Cleveland, Ohio 44121

Bonnie J. McBride and Frank J. Zeleznik
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

An addition to the computer program of NASA SP-273 is given that permits transport property calculations for the gaseous phase. Approximate mixture formulas are used to obtain viscosity and frozen thermal conductivity. Reaction thermal conductivity is obtained by the same method as in NASA TN D-7056. Transport properties for 154 gaseous species have been selected for use with the program.

INTRODUCTION

An option for calculating the dilute-gas transport properties of complex chemical mixtures has been added to the chemical equilibrium program of reference 1. Computer programs for calculating mixture transport properties are presently available (e.g., ref. 2). Reference 2 gives transport properties in the form of collision integrals and uses the Hirschfelder "rigorous" method (ref. 3) for the viscosity and thermal conductivity of nonreacting mixtures. The Brokaw method (refs. 4 and 5) is used for the contribution of chemical reaction to thermal conductivity. The objectives are (1) to use a method for calculating nonreacting (frozen) mixture properties which is simpler than that presented in reference 2, while still retaining the same accuracy, and (2) to use a simpler representation for the properties of pure species and their binary interactions. These objectives should substantially reduce calculation times or increase the size of the system which can be calculated economically.

In the new program transport properties for pure species and several binary interactions are represented in the functional form suggested in reference 6. (See the section "Transport-Property Dataset.") Mixture viscosity is obtained by an approximate method in a form first proposed by Sutherland (ref. 7). Mixture frozen thermal conductivity is obtained by an approximate method in the form first proposed by Wassiljewa (ref. 8), which is similar to Sutherland's form for viscosity. Reaction thermal conductivity is obtained in the same manner as in reference 2. The total thermal conductivity of the mixture is the sum of the frozen and reaction thermal conductivities.

This report does not repeat the material presented in reference 1 (such as the equations and numerical techniques for obtaining chemical equilibrium compositions, mixture thermodynamic properties, and various applications of these properties). Only additional material relating to transport properties is given.
APPROXIMATE MIXTURE METHODS

Sources of Approximate Methods

In addition to the "rigorous" method for obtaining the mixture transport properties mentioned in the INTRODUCTION, numerous approximate methods may be found in the literature. Some approximate methods for mixture viscosity are described in references 7 and 9 to 14, while some approximate methods for mixture frozen thermal conductivity may be found in references 8, 12, and 15 to 20. Most of these approximate methods have forms similar to those first proposed by Sutherland for viscosity (ref. 7) and by Wassiljewa for thermal conductivity (ref. 8), which can be written as

\[ \eta_{\text{mix}} = \sum_{j=1}^{n} x_j \eta_j \]  \hspace{1cm} (1)

and

\[ \lambda_{\text{mix,fr}} = \sum_{j=1}^{n} x_j \lambda_j \]  \hspace{1cm} (2)

where

- \( n \): number of gaseous species for transport calculations
- \( x_i \): mole fraction of species \( i \)
- \( \eta_i \): viscosity of species \( i \)
- \( \eta_{\text{mix}} \): viscosity of mixture
- \( \lambda_i \): thermal conductivity of species \( i \)
- \( \lambda_{\text{mix,fr}} \): thermal conductivity of mixture
- \( \varphi_{ij} \): viscosity interaction coefficient between species \( i \) and \( j \) \((\varphi_{ij} \neq \varphi_{ji})\)
- \( \psi_{ij} \): frozen-thermal conductivity interaction coefficient between species \( i \) and \( j \) \((\psi_{ij} \neq \psi_{ji})\)

The approximate methods of this type differ only in the expressions for \( \varphi_{ij} \) and \( \psi_{ij} \). For example, Hirschfelder's first approximation to his "rigorous" method for mixture viscosity contains an expression for the \( \varphi_{ij} \) in equation (1) which is used by some other authors as a starting point for deriving other approximations to \( \varphi_{ij} \). Hirschfelder's expression (ref. 3, eq. (8.3-15)) is equivalent to...
\[ \phi_{1j} = \frac{2 n_1 M_1 M_j}{n_{1j}(M_1 + M_j)^2} \left( \frac{5}{3A_{1j}^*} + \frac{M_j}{M_1} \right) \] (3)

where \( M_1 \) is the molecular weight of species 1, \( A_{1j}^* \) is a ratio of collision integrals (defined in ref. 3, eq. (8.2-15)), and \( n_{1j} \) is a quantity which can be defined in several ways, some of which are discussed later. Various expressions for \( \phi_{1j} \) derived by other investigators from equation (3) or by independent analysis can be put in the following general form for the purpose of comparison:

\[ \phi_{1j} = k_{1j} m_{1j}^r \] (4)

where

\[ m_{1j} = \frac{2M_j}{M_1 + M_j} \] (5)

and where \( r \) is an exponent and \( k_{1j} \) is a function having several forms.

Two examples are given to illustrate equation (4). For the first example, Brokaw (ref. 12) gives an expression for \( \phi_{1j} \) which is equivalent to the following:

\[ \phi_{1j} = \frac{n_1}{n_{1j}} m_{1j} \] (6)

In this case \( r = 1 \) and

\[ k_{1j} = \frac{n_1}{n_{1j}} \] (7)

As a second example, Wilke (ref. 11) gives the following expression for \( \phi_{1j} \):

\[ \phi_{1j} = \frac{1}{4} \left[ 1 + \left( \frac{n_1}{n_{1j}} \right)^{1/2} \left( \frac{M_j}{M_1} \right)^{1/4} \right]^2 m_{1j}^{1/2} \] (8)

In this case

\[ k_{1j} = \frac{1}{4} \left[ 1 + \left( \frac{n_1}{n_{1j}} \right)^{1/2} \left( \frac{M_j}{M_1} \right)^{1/4} \right]^2 \] (9)

and \( r = 1/2 \).
A summary of \( \varphi_{1j} \) for several approximate methods is given in Table I. These methods differ from one another only in the exponent \( r \). The quantity \( \eta_{1j} \) which appears in equation (6) can be obtained in several ways as follows.

An expression for \( \eta_{1j} \) is given by Hirschfelder (ref. 3, eq. (8.2-21)):

\[
\eta_{1j} \times 10^7 = \frac{26.696 \sqrt{M_1 \Omega_{1j}^{(2,2)}}}{\sigma_{1j}^2 \Omega_{1j}^{(2,2)}}
\] (10a)

where \( \Omega_{1j}^{(2,2)} \) is a collision integral and a function of \( c_{1j} \), and \( \sigma_{1j} \) and \( c_{1j} \) are Lennard-Jones interaction-potential parameters for species 1 and 1.

For \( 1 = j \), equation (10a) reduces to the following form for pure species:

\[
\eta_1 \times 10^7 = \frac{26.696 \sqrt{M_1 \Omega_1^{(2,2)}}}{\sigma_1^2 \Omega_1^{(2,2)}}
\] (10b)

where \( \eta_1 = \eta_{11} \), \( c_1 = c_{11} \), and \( \Omega_1^{(2,2)} = \Omega_1^{(2,2)} \). Hirschfelder suggests the following approximations for \( \sigma_{1j} \) and \( c_{1j} \):

\[
\sigma_{1j} = \frac{\sigma_1 + \sigma_j}{2}
\] (11)

\[
c_{1j} = \sqrt{c_1 c_j}
\] (12)

An alternative expression for \( \eta_{1j} \) can be derived based on the following approximation for \( \hat{\Omega}_{1j} \), given by Svehla and McBride (ref. 2, eq. (36)):

\[
\hat{\Omega}_{1j} = \frac{1}{4} \left( \hat{\Omega}_{11} + 2 \sqrt{\hat{\Omega}_{11} \hat{\Omega}_{jj} + \hat{\Omega}_{jj}^2} \right) \left( \sqrt{\frac{\hat{\Omega}_{11} + \hat{\Omega}_{jj}}{2}} \right)^2
\] (13)

where

\[
\hat{\Omega}_{1j} = \frac{\sigma_{1j}^2}{\Omega_{1j}} \Omega_{1j}^{(2,2)}
\] (14)

The expression for \( \eta_{1j} \) derived from equations (10a), (10b), and (13) is

\[
\eta_{1j} = \frac{\eta_1 m_{1j}^{1/2}}{k_{1j}}
\] (15)
where $k_{ij}$ is defined by equation (9). Substitution of $n_{ij}$ from equation (15) into equation (6) gives the exact expression for $\psi_{ij}$ in equation (8). Thus, if the approximation given in equation (13) is used, equations (6) and (8) are identical.

In addition to equations (10a) and (15), values of $n_{ij}$ may also be derived from experimental data on mixture viscosity. These three methods for obtaining $n_{ij}$ generally give different numerical values. Therefore, even the "rigorous" method gives different values for mixture viscosity depending on what value is used for $n_{ij}$.

Expressions for $\psi_{ij}$ (refs. 12 and 15 to 19) are given in table II. The expressions from references 17 and 19 are the same as that from reference 18 except for the factors of 1.065 and 0.866. The formulas of Lindsay and Bromley (ref. 15) contain parameters known as Sutherland constants which can be estimated in various ways. Sutherland constants for this report were obtained from viscosity by means of the following formula (derived in ref. 21):

$$1 + \frac{S_1}{T} = \left(\frac{3}{2} - \frac{\ln n_1}{\ln T}\right)^{-1}$$

(16a)

The Sutherland interaction constant $S_{ij}$ was obtained from the following approximation:

$$S_{ij} = \sqrt{S_i S_j}$$

(16b)

In addition to the foregoing methods there is an "averaging" method for thermal conductivity due to Burgoyne and Weinberg (ref. 20). A generalized version of this method is

$$\lambda_{mix,fr} = \frac{1}{2} \left( \sum_{i=1}^{n} x_i \lambda_i + \frac{1}{\sum_{i=1}^{n} \frac{x_i}{\lambda_i}} \right)$$

(17)

An analogous formula for viscosity is

$$\eta_{mix} = \frac{1}{2} \left( \sum_{i=1}^{n} x_i \eta_i + \frac{1}{\sum_{i=1}^{n} \frac{x_i}{\eta_i}} \right)$$

(18)
Selection of Approximate Method

A number of mixture methods were tested to discover the extent each reproduced experimental viscosity and thermal conductivity data for several binary systems. The methods tested were the "rigorous" method; the approximate methods, whose expressions for \( \psi_{ij} \) and \( \phi_{ij} \) appear in tables I and II; and the averaging method of reference 20. All the methods reproduced the experimental data by better than 3 percent for at least some of the test cases. However, each method also produced errors exceeding 7 percent in at least one case.

An example of the spread in accuracies is shown in table III for the Ar-NH\(_3\) system using the experimental data of reference 22. The experimental data are for eight different compositions of Ar and NH\(_3\) at a temperature of 308 K. Calculations were made with values of \( \eta_{1j} \) from equations (10a) and (15) and a value of \( \eta_{1j} = 175 \) derived from experimental data. In order to derive a value from experimental data, it is necessary to select the form of the mixture equation with which it is to be used. For this example, the mixture method of reference 12 was selected with \( k_{1j} \) from equation (5) and with the exponent \( r = 1 \). As expected table III shows that the best results (average absolute error = 0.2 percent) were obtained using the method of Brokaw (ref. 12) and the \( \eta_{1j} \) derived from experimental data with the same method.

For the binary systems tested, comparisons with experimental data showed that no one method of calculation could be judged superior to all others in all cases. The selection of a particular method represents a compromise between overall accuracy and ease of computations. To obtain viscosity of mixtures, the expression for \( \phi_{ij} \) from equation (6) is used in equation (1) if values of \( \eta_{1j} \) are available in the dataset discussed in the section "Transport-Property Dataset". Otherwise \( \phi_{ij} \) from equation (8) is used (which implies using a value of \( \eta_{1j} \) from eq. (15)).

Brokaw's mixture method for frozen thermal conductivity (ref. 16) was selected inasmuch as it reproduced the experimental data for the test cases slightly better than the other methods tried. The same values used for \( \phi_{ij} \) for viscosity are also used to calculate \( \psi_{ij} \) for frozen thermal conductivity. Reaction thermal conductivity is obtained by the same method as used in reference 2.

COMPUTER PROGRAM FOR TRANSPORT PROPERTIES

The computer program was written in FORTRAN IV and tested on an IBM 370/3033 Computer at the Lewis Research Center. A logical variable TRNSPT, was added to NAMELIST/INPT2/ of reference 1. Transport calculations are carried out only if TRNSPT = T has been included in the namelist input. Table IV lists the I/O (Input/Output) units used by the program. A transport-property dataset, five subroutines, and BLOCK DATA are involved in transport-property calculations.

One of the five subroutines, SEARCH, has two purposes. One purpose is to search the unformatted thermodynamic data on I/O unit 4 for all possible
species in any specified chemical system and to store thermodynamic coeffi-
cients for these possible species in a COMMON block. A second purpose, if
THNSP1 = 1, is to search the unformatted transport data on I/O unit 8 for all
possible species in any specified chemical system and to store transport coef-
cients for these species on I/O unit 3. Subroutines TRANP and INPUT and the
entry OUT4 in subroutine OUT1 are used exclusively for transport-property cal-
culations. BLOCK DATA contains headings for transport property output as well
as other information required by the program. The fifth subroutine, UTRAN, is
used only for converting formatted transport properties to an unformatted form.

Transport-Property Dataset

Transport properties for 154 pure species and several binary viscosity
interaction quantities \( n_{ij} \) were least-squares fitted to the following form,
used in reference 6:

\[
\begin{align*}
\ln \eta &= A \ln T + \frac{B}{T} + \frac{C}{T^2} + D \\
\ln \lambda &= \frac{E}{T^2} + F
\end{align*}
\]  

(19)

The coefficients were generated to give viscosity in units of \( \mu \)P and thermal
conductivity in units of \( \mu \)W/cm K. The temperature range was divided into two
intervals to be consistent with the same intervals selected for thermodynamic
properties, namely, 300 to 1000 K and 1000 to 5000 K (although the program
permits any three intervals for any species). Therefore, in the present data-
set, each pure species or binary interaction may have four sets of coeffi-
cients: two sets for viscosity (high- and low-temperature intervals) and two
sets for thermal conductivity (high- and low-temperature intervals). If only
viscosity or only thermal conductivity is present, only the two sets of coeffi-
cients for that property are given. The code word TRAN must precede the
formatted sets of coefficients, and the code word LAST must follow. The format
for the dataset containing these coefficients is given in table V.

Subroutine UTRAN

Coefficients for generating thermodynamic and transport properties are used
by the program in an unformatted form in order to reduce computer time consid-
erably. Conversion of the coefficients for transport properties from formatted
to unformatted form is done by subroutine UTRAN. The formatted coefficients
are read in as input on I/O unit 5. Subroutine UTRAN converts the formatted
coefficients and writes them in the unformatted form on I/O unit 8. After
conversion, the coefficients are available for future runs in unformatted form
on I/O unit 8, and subroutine UTRAN need not be used again until the formatted
dataset is revised.

Subroutine INPUT

After composition has been determined for a specified thermodynamic data
point (such as an assigned temperature and pressure), subroutine INPUT
selects coefficients for a maximum of the 50 most abundant gaseous species for
that point from among the transport coefficients previously stored on I/O
unit 3. Depending on the accuracy desired, the number of species used by the program may often be reduced by means of an optional input parameter TRPACC. If, for example, TRPACC is set equal to 0.98, the program will consider only those species which add up to 0.98 of the total molar composition (adding in the order of largest to smallest species mole fraction). The default value of TRPACC is 0.99995. The mole fractions of these selected species are first normalized to give a total of 1.0 before mixture transport properties are calculated. The transport properties are calculated from the selected coefficients at the current temperature.

Subroutine TRANP

Subroutine TRANP sets up the equations and solves for mixture viscosity, frozen thermal conductivity, equilibrium thermal conductivity, and equilibrium specific heat. The method and equations for obtaining equilibrium specific heat and the reaction contribution to thermal conductivity are given in reference 2.

Entry OUT4 in Subroutine OUT1

Entry OUT4 handles the output of the transport-property calculations. A variable format is used which is the same as the format used for thermodynamic-properties output (described in ref. 1).

DESCRIPTION OF PROGRAM OUTPUT

A sample problem containing transport-property output is given in table VI. Transport properties are given for mixtures of gases only. Therefore, for mixtures containing condensed species, two values of equilibrium specific heat are given. One value (which includes gaseous and condensed-species contributions) is given with the output labeled THERMODYNAMIC PROPERTIES, while a second value (which contains only gaseous-species contributions) is given with the output labeled TRANSPORT PROPERTIES. For each point a maximum of the 50 most abundant gaseous species is used for calculating mixture transport properties. Thermal conductivities are given for the assumptions of both equilibrium and frozen gaseous compositions. Viscosity is always given in units of mP. An option is provided in the namelist input for units of thermodynamic properties. Units for thermal conductivity are consistent with the option selected for thermodynamic units. That is, thermal conductivity is in units of mW/cm sec if SIUNIT = T is included in the input dataset and mcal/cm K sec otherwise. The Prandtl number has the usual definition of \( C_p \tau \lambda / \lambda \), while the Lewis number as defined in reference 2, is

\[
Le = \frac{\lambda_{\text{reac}} C_p \rho \tau}{\lambda_{\text{fr}} C_p \rho_{\text{reac}}}
\]

(20)
SELECTION OF TRANSPORT PROPERTIES

Sources of Properties for Pure Species

Transport properties for all species except those discussed in the following paragraphs were taken from the compilations of Svehla (ref. 23). For several species thermal conductivities were calculated for this report from viscosities by means of the following equations, given in reference 2:

\[ \lambda_{tr,1} = \frac{15}{4} \frac{R}{M_1} n_1 \]  
(21)

\[ \lambda_{int,1} = \frac{R}{M_1} n_1 \left[ \frac{6}{5} A_{11}^* C_{int,1} - \frac{C_{rot,1}}{2^{rot,1}} \left( \frac{5}{2} - \frac{6}{5} A_{11}^* \right) \right] \]  
(22)

\[ \lambda_1 = \lambda_{tr,1} + \lambda_{int,1} \]  
(23)

where

\[ C_{int,1} = \frac{C_p,1}{R} - \frac{5}{2} \]  
(24)

and

\[ C_{rot,1} = \frac{C_p,rot,1}{R} \]  
(25)

For atomic species, \( \lambda_{int,1} = 0 \) and \( \lambda_1 = \lambda_{tr,1} \). \( C_{rot,1} \) is assumed to be 1 for linear species and 1.5 for nonlinear species.

Argon. - References 6, 24, and 25 contain critical reviews of viscosity data for Ar. References 6 and 25 include more recently available experimental viscosity data in their evaluation than found in reference 24. Additionally, recommended values from references 6 and 25 are in close agreement (less than 1 percent difference from 200 to 2000 K). By contrast, the values of reference 24 agree with values from reference 25 at room temperature but differ by 8.5 percent at 2000 K. Viscosities and thermal conductivities were taken from reference 25 in order to have a consistent set of values.

Atomic carbon. - Collision integrals are given in reference 26 for every 1000 K from 1000 to 25 000 K. These collision integrals were extrapolated down to 300 K and converted to viscosities. Thermal conductivities were obtained by means of equation (21).

Methane. - Viscosities selected by references 6, 24, and 27 to 30 are all in extremely close agreement (less than 1 percent difference). The temperature range for viscosity in these references is from 200 to 1000 K, although
not every reference covers the entire range. The average of viscosities in these six references was selected. Thermal conductivities were selected to be the average of the values from references 27 and 30 to 32.

**Carbon monoxide.** - Viscosities from references 24, 27, 33, and 34 were reviewed. The values selected by reference 27 are about 2 to 3 percent lower than those of the other three references in the range from 500 to 1000 K and were not used. The averaged values from the other three references are extremely close to the N₂ viscosity values of reference 35. The reference 35 N₂ values were therefore selected as the viscosity for CO inasmuch as the N₂ values are given to 2000 K. Thermal conductivities were selected to be the average of the values in the four references 27, 31, 33, and 36.

**Carbon dioxide.** - Viscosities from the five references 6, 24, 27, 37, and 38 were reviewed. Only those of references 6 and 38 were used to obtain average values. The values in reference 37 were not used because, according to figure 3 in that reference, the calculated values appear to be about 0.5 to 2 percent too high from 400 to 800 K. The older values of references 24 and 27 were not used because they appear to be about 4 percent lower than the more recent values in references 6 and 38. Thermal conductivities were averaged from those given in the five references 27, 31, and 39 to 41.

**Atomic hydrogen.** - High-temperature viscosities (above 1000 K) were calculated from the collision integrals given in reference 18. Low-temperature viscosities (200 to 500 K) were taken from reference 42. Values from 500 to 1000 K were interpolated. Thermal conductivities were calculated by means of equation (21).

**Molecular hydrogen.** - Viscosities of H₂ were taken to be the average of the values in the four references 6, 24, 27, and 43. Thermal conductivities from the four references 27, 31, 40, and 43 were reviewed. The selected values are as follows: from 200 to 600 K, average values from the four references; from 1100 to 5000 K, reference 43 values; from 700 to 1000 K, values "faired" between the other selected values.

**Water.** - Viscosities and thermal conductivities from 373 to 1073 K were taken from reference 44 and extrapolated to higher temperatures by means of equations given in reference 45.

**Atomic nitrogen.** - The high-temperature (1000 to 15 000 K) collision integrals given in reference 46 were converted to viscosities and extrapolated to lower temperatures. Thermal conductivities were obtained by means of equation (21).

**Ammonia.** - Viscosities were selected to be the averages of those given in references 23, 24, and 47. Thermal conductivities were selected to be the average of those in references 27, 31, 48, and 49.

**Nitric oxide.** - The two sets of viscosities and thermal conductivities for NO from references 2 and 24 are fairly close. The reference 2 viscosities were selected inasmuch as a least-squares fit of these values gave less error than a similar fit of the reference 24 values. The reference 2 thermal conductivities were selected in order to be consistent with the viscosities. The selected transport properties are also given in reference 50.
Nitrogen dioxide. - A problem in obtaining transport properties for NO₂ lies in the fact that there is considerable association of NO₂ to N₂O₄ in the temperature region of about 300 to 400 K. Thus experimental data are open to interpretation as to whether measurements are for the pure species, an equilibrium mixture of NO₂ and N₂O₄, or some other combination of the two species. References 24 and 51 interpret the experimental data of reference 52 differently. There is close agreement for temperatures above 400 K (where the equilibrium mixture is 98 percent NO₂) but considerable difference otherwise. Inasmuch as reference 51 obtained viscosity data for NO₂ and N₂O₄ simultaneously from the reference 52 values, those results were selected for viscosity. Thermal conductivities were obtained from viscosities by means of equations (21) to (23) with \( Z_{\text{rot}} = \infty \).

Diatomic nitrogen. - A comparison was made among the critically evaluated and selected viscosities given in the three references 6, 24, and 35. The agreement between the data from references 6 and 35 is excellent (only a few tenths of a percent difference in the entire temperature range from 200 to 2000 K). Reference 24 is in good agreement with the others at low temperatures but differs by as much as 8 percent at 2000 K. Viscosities and thermal conductivities were taken from reference 35 inasmuch as reference 6 does not contain thermal conductivities.

Nitrous oxide. - Viscosities from references 2 and 24 for N₂O are very close (less than 0.6 percent difference from 200 to 1000 K). The reference 2 values were selected since they are given to 5000 K. The thermal conductivities from reference 31 appear to be closer to the experimental data than do those in reference 2 and also closer to one recent value given in reference 53. The reference 31 thermal conductivities were selected up to 700 K. Above 700 K they were calculated from viscosities by means of equations (21) to (23) with \( Z_{\text{rot}} = \infty \).

Atomic oxygen. - Two sets of high-temperature viscosities were compared (refs. 27 and 46). These agree to within 2.5 percent from 3000 to 5000 K. The viscosities of reference 46 were selected since these are given from 1000 to 5000 K, whereas the reference 27 values are given only above 3000 K. Low-temperature viscosities (200 to 300 K) were taken from reference 54. Viscosities from 400 to 900 K were interpolated. Thermal conductivities were obtained by means of equation (21).

Molecular oxygen. - Viscosities from references 6, 24, 27, and 35 were reviewed. The averages of these viscosities are within 1 percent of the reference 35 values. The reference 35 values were selected. Thermal conductivities from references 27, 31, 35, 55, and 56 were reviewed. The averages of these agree to within 1 percent with reference 35 from 200 to 600 K, but differ more at higher temperatures (3 percent from 1000 to 1300 K). According to Hanley (ref. 35), "...most of the data for the thermal conductivity coefficient for both nitrogen and oxygen seem unreliable outside the range of 150 to 600 K." Thermal conductivities were also taken from reference 35 to be consistent with the selected viscosities.

Hydroxyl radical. - Experimental transport data for the OH radical are not available. The collision integrals estimated in reference 57 and the rotational collision number \( Z_{\text{rot}} = 8 \) estimated in reference 2 were used to calculate viscosities and thermal conductivities.
Sources of Properties for Binary Interactions

The transport-property dataset currently provides coefficients for obtaining $n_{1j}$ for only three pairs. These coefficients were taken directly from reference 58. Values of $n_{ij}$ for other pairs are estimated in the program by means of equation (15) using $k_{ij}$ from equation (9).
APPENDIX - SYMBOLS

A, B, C, D coefficients in eq. (19)

$A_{ij}^*, A_{ij}^*$ ratio of collision integrals, dimensionless

$C_p$ constant-pressure heat capacity, J/kmol K

$C_{\text{int},1}$ term defined by eq. (24), dimensionless

$C_{\text{rot},1}$ term defined by eq. (25), dimensionless

$C_p$ constant-pressure specific heat, J/kg K

$D_1$ self-diffusion coefficient, m$^2$/sec

$D_{ij}$ binary diffusion coefficient, m$^2$/sec

$k_{ij}$ function defined by eq. (7) or (9), dimensionless

$Le$ Lewis number, defined by eq. (20), dimensionless

$M_1$ molecular weight of species 1, kg/kmol

$m_{ij}$ molecular weight function defined by eq. (5), dimensionless

$n$ number of gaseous species included in transport calculations, dimensionless

$R$ universal gas constant, 8314.41 J/kmol K

$r$ exponent in eq. (4)

$S_i$ Sutherland constant for species i, K

$S_{ij}$ Sutherland interaction constant for species i and j, K

$t$ temperature, K

$x_i$ mole fraction of species i, dimensionless

$Z_{\text{rot}}$ rotational collision number

$e_i$ depth of potential energy well for species i, J

$e_{ij}$ quantity defined by eq. (12)

$n_i$ viscosity, kg/m sec

$\eta_i$ viscosity of species i, kg/m sec

$\eta_{ij}$ quantity defined by eqs. (10a) and (15), kg/m sec

$\lambda$ thermal conductivity, W/m K

$\lambda_i$ thermal conductivity for species i, W/m K

$\lambda_{ij}$ quantity in table II, W/m K

$\sigma_i$ molecular diameter for species i, A

$\sigma_{ij}$ quantity defined in eq. (11), A

$\phi_{ij}$ viscosity interaction coefficient (eq. (6) or (8)), dimensionless

$\psi_{ij}$ frozen-thermal-conductivity interaction coefficient (eq. (2) and table II), dimensionless

$a_{ij}^{(2,2)*}$ collision integral, dimensionless
\( \Omega_{ij} \)  
collision cross section defined in eq. (14), \( \text{A}^2 \)

Subscripts:
- \( \text{fr} \): frozen contribution
- \( i,j \): index for species
- \( \text{int} \): internal contribution
- \( \text{mix} \): for the mixture
- \( \text{reac} \): chemical reaction contribution
- \( \text{rot} \): rotational contribution
- \( \text{tr} \): translational contribution
REFERENCES


### TABLE I. - EXPRESSIONS FOR $\varphi_{ij}$ FOR MIXTURE VISCOSITY

<table>
<thead>
<tr>
<th>Reference</th>
<th>Original expression for $\varphi_{ij}$ given in reference</th>
<th>Exponent $r$ in $\varphi_{ij} = k_{ij} m_{ij}^r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(eq. (4))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>For $k_{ij} =$ $\frac{n_i}{n_{ij}}$ (eq. (7))</td>
</tr>
<tr>
<td><strong>Wilke, ref. 11</strong></td>
<td>$\frac{1}{4} \left[ 1 + \left( \frac{n_i}{n_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2 m_{ij}^{1/2}$</td>
<td>$1/2$</td>
</tr>
<tr>
<td><strong>Brokaw, ref. 12</strong></td>
<td>$\frac{D_i}{D_{ij}} \frac{A_{ij}}{A_i} = \frac{\lambda_i}{\lambda_{ij}} = \frac{n_i}{n_{ij}} m_{ij}$</td>
<td>$1$</td>
</tr>
<tr>
<td><strong>Brokaw, ref. 12</strong></td>
<td>$\frac{\lambda_i}{\lambda_{ij}} m_{ij}^{-1/8}$</td>
<td>$7/8$</td>
</tr>
<tr>
<td><strong>Francis, ref. 13</strong></td>
<td>$\frac{\bar{a}_{ij}}{\bar{a}<em>i} m</em>{ij}^{1/3}$</td>
<td>$5/6$</td>
</tr>
<tr>
<td><strong>Sutherland, ref. 7</strong></td>
<td>$\frac{\bar{a}_{ij}}{\bar{a}<em>j} m</em>{ij}^{1/4}$</td>
<td>$3/4$, $1/4$</td>
</tr>
<tr>
<td>Reference</td>
<td>( \psi_{ij} )</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Lindsay and Bromley, ref. 15</td>
<td>( \frac{1}{4} \left( 1 + \left( \frac{n_i}{n_j} \left( \frac{M_j}{M_i} \right) \right)^{3/4} \left( \frac{1 + \frac{S_{ij}}{S_i}}{1 + \frac{S_{ij}}{S_j}} \right)^2 \right) )</td>
<td></td>
</tr>
<tr>
<td>Brokaw, ref. 12</td>
<td>( \psi_{ij} \left[ 1 + \left( \frac{M_i - M_j}{M_i + M_j} \right)^2 \left( \frac{15}{4A_{ij}} - 1 \right) \left( 1 + \frac{128^2_{ij} + 5}{30 - 8A_{ij}} \frac{M_j}{M_i - M_j} \right) \right] )</td>
<td></td>
</tr>
<tr>
<td>Brokaw, ref. 12</td>
<td>( \psi_{ij} \left[ 1 + \frac{2.54(M_i - M_j)(M_i - 0.177 M_j)}{(M_i + M_j)^2} \right] )</td>
<td></td>
</tr>
<tr>
<td>Brokaw, ref. 16</td>
<td>( \psi_{ij} \left[ 1 + \frac{2.41(M_i - M_j)(M_i - 0.142 M_j)}{(M_i + M_j)^2} \right] )</td>
<td></td>
</tr>
<tr>
<td>Mason and Saxena, ref. 17</td>
<td>( 1.065 \left( \frac{1}{4} m_{ij}^{1/2} \left[ 1 + \left( \frac{\lambda_i}{\lambda_j} \right)^{1/2} \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2 \right) )</td>
<td></td>
</tr>
<tr>
<td>Vanderslice et al., ref. 18</td>
<td>( \frac{1}{4} m_{ij}^{1/2} \left[ 1 + \left( \frac{\lambda_i}{\lambda_j} \right)^{1/2} \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2 )</td>
<td></td>
</tr>
<tr>
<td>Tondor and Saxena, ref. 19</td>
<td>( 0.866 \left( \frac{1}{2} m_{ij}^{1/2} \left[ 1 + \left( \frac{\lambda_i}{\lambda_j} \right)^{1/2} \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2 \right) )</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE III. - AVERAGE ABSOLUTE PERCENT ERROR FOR Ar-NH₃**

[Comparison of eight experimental mixture viscosities from ref. 22 with corresponding calculated values.]

<table>
<thead>
<tr>
<th>Method of calculation</th>
<th>Average absolute percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \eta_{ij} = 148.2 ) (eq. (15))</td>
</tr>
<tr>
<td>Hirschfelder &quot;rigorous&quot; (ref. 3)</td>
<td>8.1</td>
</tr>
<tr>
<td>Wilke (ref. 11)</td>
<td>5.8</td>
</tr>
<tr>
<td>Brokaw (r = 1) (ref. 12)</td>
<td>5.8</td>
</tr>
<tr>
<td>Brokaw (r = 7/8) (ref. 12)</td>
<td>6.9</td>
</tr>
<tr>
<td>Francis (ref. 13)</td>
<td>7.3</td>
</tr>
<tr>
<td>Sutherland (ref. 7)</td>
<td>8.0</td>
</tr>
<tr>
<td>Burgoyne (ref. 20)</td>
<td>12.5</td>
</tr>
</tbody>
</table>

*Method does not use \( \eta_{ij} \).*
TABLE IV. - INPUT/OUTPUT DATA FILES

<table>
<thead>
<tr>
<th>I/O unit</th>
<th>Data file</th>
</tr>
</thead>
</table>
| 3        | Scratch unit  
          | (1) Used during conversion of formatted to unformatted data  
          | (2) Unformatted coefficients to generate transport properties for a particular chemical system |
| 4        | Unformatted coefficients to generate thermodynamic properties for all species |
| 5        | Formatted input. Case input (described in ref. 1) and formatted coefficients to generate thermodynamic and transport properties:  
          | (Note: Formatted coefficients need to be processed only once. Program will write the unformatted files 4 and 8.) |
| 6        | Output |
| 8        | Unformatted coefficients to generate transport properties for all species and pairs of species |
### TABLE V. - FORMAT FOR TRANSPORT-PROPERTY DATASET

<table>
<thead>
<tr>
<th>Number of cards</th>
<th>Contents</th>
<th>Format</th>
<th>Card columns</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TRAN (indicates beginning of transport-property dataset)</td>
<td>A4</td>
<td>1 to 4</td>
</tr>
<tr>
<td>a1</td>
<td>Species name</td>
<td>4A4</td>
<td>1 to 16</td>
</tr>
<tr>
<td></td>
<td>Second species name if binary interaction, blank for pure species</td>
<td>4A4</td>
<td>17 to 32</td>
</tr>
<tr>
<td></td>
<td>V if there are viscosity coefficients</td>
<td>A1</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Temperature intervals for viscosity (0,1,2, or 3)</td>
<td>I1</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>C if there are thermal conductivity coefficients</td>
<td>A1</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Temperature intervals for thermal conductivity (0,1,2, or 3)</td>
<td>I1</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Comments-references, date, etc.</td>
<td>10A4</td>
<td>41 to 80</td>
</tr>
<tr>
<td>bAny number</td>
<td>Blank</td>
<td>1X</td>
<td>1</td>
</tr>
<tr>
<td>from 1 to 6</td>
<td>V if coefficients are for viscosity</td>
<td>A1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>C if coefficients are for thermal conductivity</td>
<td>A1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>First and last temperature of temperature interval</td>
<td>2F9.2</td>
<td>3 to 20</td>
</tr>
<tr>
<td></td>
<td>Four coefficients in eq. (19)</td>
<td>4E15.8</td>
<td>21 to 80</td>
</tr>
<tr>
<td>1</td>
<td>LAST (indicates end of transport-property dataset)</td>
<td>A4</td>
<td>1 to 4</td>
</tr>
</tbody>
</table>

aHeader card for each pure species or binary interaction.
bThe number of cards for each pure species or binary interaction equals the sum of the number of temperature intervals for both viscosity and thermal conductivity (sum of the numbers in columns 36 and 38 of the header card). Temperature intervals must be in increasing order. Viscosity or thermal conductivity order is immaterial. Any number of species is permitted between the first card (TRAN) and last card (LAST).
### TABLE VI. THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURE AND PRESSURE

<table>
<thead>
<tr>
<th>CASE NO.</th>
<th>6667</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMICAL FORMULA</td>
<td></td>
</tr>
<tr>
<td>FUEL</td>
<td>H 2.00000</td>
</tr>
<tr>
<td>OXIDANT</td>
<td>O 2.00000</td>
</tr>
</tbody>
</table>

| O/F | 7.9370 |
| PERCENT FUEL | 11.1894 |
| EQUIVALENCE RATIO | 1.0000 |
| PHI | 1.0000 |

#### THERMODYNAMIC PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P, MPa</td>
<td>0.10132</td>
</tr>
<tr>
<td>T, DEG K</td>
<td>5000.0</td>
</tr>
<tr>
<td>RXD KG/GM M</td>
<td>1.4967-2</td>
</tr>
<tr>
<td>H, KJ/KG</td>
<td>52669.0</td>
</tr>
<tr>
<td>G, KJ/KG</td>
<td>-107511.2</td>
</tr>
<tr>
<td>S, KJ/(KG)(K)</td>
<td>32.0360</td>
</tr>
<tr>
<td>M, MOL WT</td>
<td>6.141</td>
</tr>
<tr>
<td>(DLV/DLP)T</td>
<td>-1.02147</td>
</tr>
<tr>
<td>(DLV/DLP)P</td>
<td>1.2519</td>
</tr>
<tr>
<td>CP, KJ/(KG)(K)</td>
<td>7.2044</td>
</tr>
<tr>
<td>GAMMA (S)</td>
<td>1.3668</td>
</tr>
<tr>
<td>SON VEL.M/SEC</td>
<td>3041.9</td>
</tr>
</tbody>
</table>

#### TRANSPORT PROPERTIES (GASES ONLY)

| Conductivity in Units of Milliwatts/(CM)(K) |       |
| VISC. MILLIPOISE | 1.2746 |
| LEWIS NUMBER | 0.6776 |

#### WITH EQUILIBRIUM REACTIONS

| CP, KJ/(KG)(K) | 7.2044 |
| CONDUCTIVITY | 16.5206 |
| PRANDTL NUMBER | 0.5558 |

#### WITH FROZEN REACTIONS

| CP, KJ/(KG)(K) | 3.5100 |
| CONDUCTIVITY | 9.6433 |
| PRANDTL NUMBER | 0.4639 |

#### MOLE FRACTIONS

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.65095</td>
</tr>
<tr>
<td>H2O</td>
<td>0.01037</td>
</tr>
<tr>
<td>O</td>
<td>0.32663</td>
</tr>
<tr>
<td>OH</td>
<td>0.00567</td>
</tr>
<tr>
<td>O2</td>
<td>0.00219</td>
</tr>
</tbody>
</table>

#### ADDITIONAL PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS WERE LESS THAN 0.000005 FOR ALL ASSIGNED CONDITIONS

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O2</td>
<td>0.03</td>
</tr>
<tr>
<td>H2O(S)</td>
<td></td>
</tr>
<tr>
<td>H2O(L)</td>
<td></td>
</tr>
</tbody>
</table>