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

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COMPUTER PROGRAM FOR CALCULATION OF COMPLEX CHEMICAL
EQUILIBRIUM COMPOSITIONS AND APPLICATIONS
SUPPLEMENT I - TRANSPORT PROPERTIES

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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.

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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

$$\eta_{mix} = \sum_{i=1}^n \frac{x_i \eta_i}{x_i + \sum_{\substack{j=1 \\ j \neq i}}^n x_j \varphi_{ij}} \quad (1)$$

and

$$\lambda_{mix,fr} = \sum_{i=1}^n \frac{x_i \lambda_i}{x_i + \sum_{\substack{j=1 \\ j \neq i}}^n x_j \psi_{ij}} \quad (2)$$

where

- n number of gaseous species for transport calculations
- x_i mole fraction of species i
- η_i viscosity of species i
- η_{mix} viscosity of mixture
- λ_i thermal conductivity of species i
- $\lambda_{mix,fr}$ frozen-thermal conductivity of mixture
- φ_{ij} viscosity interaction coefficient between species i and j ($\varphi_{ij} \neq \varphi_{ji}$)
- ψ_{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 φ_{ij} and ψ_{ij} . For example, Hirschfelder's first approximation to his "rigorous" method for mixture viscosity contains an expression for the φ_{ij} in equation (1) which is used by some other authors as a starting point for deriving other approximations to φ_{ij} . Hirschfelder's expression (ref. 3, eq. (8.2-26)) is equivalent to

$$\varphi_{1j} = \frac{2 n_1 M_1 M_j}{n_{1j} (M_1 + M_j)^2} \left(\frac{5}{3A_{1j}^*} + \frac{M_1}{M_1} \right) \quad (3)$$

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 φ_{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:

$$\varphi_{1j} = k_{1j} m_{1j}^r \quad (4)$$

where

$$m_{1j} = \frac{2M_1}{M_1 + M_j} \quad (5)$$

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 φ_{1j} which is equivalent to the following:

$$\varphi_{1j} = \frac{n_1}{n_{1j}} m_{1j} \quad (6)$$

In this case $r = 1$ and

$$k_{1j} = \frac{n_1}{n_{1j}} \quad (7)$$

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

$$\varphi_{1j} = \frac{1}{4} \left[1 + \left(\frac{n_1}{n_j} \right)^{1/2} \left(\frac{M_1}{M_j} \right)^{1/4} \right]^2 m_{1j}^{1/2} \quad (8)$$

In this case

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

and $r = 1/2$.

A summary of φ_{ij} for several approximate methods is given in table I. These methods differ from one another only in the exponent r . The quantity η_{ij} which appears in equation (6) can be obtained in several ways as follows.

An expression for η_{ij} is given by Hirschfelder (ref. 3, eq. (8.2-21)):

$$\eta_{ij} \times 10^7 = \frac{26.696 \sqrt{\frac{2M_1 M_2 T}{(M_1 + M_2)}}}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}} \quad (10a)$$

where $\Omega_{ij}^{(2,2)*}$ is a collision integral and a function of ϵ_{ij} , and σ_{ij} and ϵ_{ij} are Lennard-Jones interaction-potential parameters for species 1 and j. For $i = j$, equation (10a) reduces to the following form for pure species:

$$\eta_i \times 10^7 = \frac{26.696 \sqrt{M_1 T}}{\sigma_i^2 \Omega_i^{(2,2)*}} \quad (10b)$$

where $\eta_i = \eta_{ii}$, $\sigma_i = \sigma_{ii}$, and $\Omega_i^{(2,2)*} = \Omega_{ii}^{(2,2)*}$. Hirschfelder suggests the following approximations for σ_{ij} and ϵ_{ij} :

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (11)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (12)$$

An alternative expression for η_{ij} can be derived based on the following approximation for $\bar{\Omega}_{ij}$, given by Svehla and McBride (ref. 2, eq. (36)):

$$\bar{\Omega}_{ij} = \frac{1}{4} \left(\bar{\Omega}_{ii} + 2 \sqrt{\bar{\Omega}_{ii} \bar{\Omega}_{jj}} + \bar{\Omega}_{jj} \right) = \left(\frac{\sqrt{\bar{\Omega}_{ii}} + \sqrt{\bar{\Omega}_{jj}}}{2} \right)^2 \quad (13)$$

where

$$\bar{\Omega}_{ij} = \sigma_{ij}^2 \Omega_{ij}^{(2,2)*} \quad (14)$$

The expression for η_{ij} derived from equations (10a), (10b), and (13) is

$$\eta_{ij} = \frac{\eta_i m_{ij}^{1/2}}{k_{ij}} \quad (15)$$

where k_{ij} is defined by equation (9). Substitution of n_{ij} from equation (15) into equation (6) gives the exact expression for ψ_{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 ψ_{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):

$$1 + \frac{S_1}{T} = \left(\frac{3}{2} - \frac{d \ln \eta_1}{d \ln T} \right)^{-1} \quad (16a)$$

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

$$S_{ij} = \sqrt{S_i S_j} \quad (16b)$$

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

$$\lambda_{mix, fr} = \frac{1}{2} \left(\sum_{i=1}^n x_i \lambda_i + \frac{1}{\sum_{i=1}^n \frac{x_i}{\lambda_i}} \right) \quad (17)$$

An analogous formula for viscosity is

$$\eta_{mix} = \frac{1}{2} \left(\sum_{i=1}^n x_i \eta_i + \frac{1}{\sum_{i=1}^n \frac{x_i}{\eta_i}} \right) \quad (18)$$

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 φ_{1j} and ψ_{1j} 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-NH₃ system using the experimental data of reference 22. The experimental data are for eight different compositions of Ar and NH₃ at a temperature of 308 K. Calculations were made with values of η_{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 (7) 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 η_{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 φ_{1j} from equation (6) is used in equation (1) if values of η_{1j} are available in the dataset discussed in the section "Transport-Property Dataset". Otherwise φ_{1j} from equation (8) is used (which implies using a value of η_{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 φ_{1j} for viscosity are also used to calculate ψ_{1j} 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 TRNSP1, 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 coefficients for these possible species in a COMMON block. A second purpose, if TRNSP1 = T, 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 coefficients 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 calculations. 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 η_{ij} were least-squares fitted to the following form, used in reference 6:

$$\left. \begin{array}{l} \ln \eta \\ \ln \lambda \end{array} \right\} = A \ln T + \frac{B}{T} + \frac{C}{T^2} + D \quad (19)$$

The coefficients were generated to give viscosity in units of μP and thermal conductivity in units of $\mu\text{W/cm K}$. 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 dataset, each pure species or binary interaction may have four sets of coefficients: 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 coefficients 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 considerably. 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 $c_{p,n}/\lambda$, while the Lewis number as defined in reference 2, is

$$Le = \frac{\lambda_{\text{reac}} c_{p,fr}}{\lambda_{fr} c_{p, \text{reac}}} \quad (20)$$

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:

$$\lambda_{tr,1} = \frac{15}{4} \frac{R}{M_1} \eta_1 \quad (21)$$

$$\lambda_{int,1} = \frac{R}{M_1} \eta_1 \left[\frac{6}{5} A_{11}^* C_{int,1} - \frac{\frac{C_{rot,1}}{Z_{rot,1}} \left(\frac{5}{2} - \frac{6}{5} A_{11}^* \right)}{\frac{\pi}{2} \left(\frac{C_{rot,1}}{Z_{rot,1}} \right) \left(\frac{5}{3} + \frac{6A_{11}^*}{5C_{int,1}} \right)} \right] \quad (22)$$

$$\lambda_1 = \lambda_{tr,1} + \lambda_{int,1} \quad (23)$$

where

$$C_{int,1} = \frac{C_{p,1}}{R} - \frac{5}{2} \quad (24)$$

and

$$C_{rot,1} = \frac{C_{p,rot,1}}{R} \quad (25)$$

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 N_2 viscosity values of reference 35. The reference 35 N_2 values were therefore selected as the viscosity for CO inasmuch as the N_2 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 H_2 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 NO_2 lies in the fact that there is considerable association of NO_2 to N_2O_4 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 NO_2 and N_2O_4 , 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 NO_2) but considerable difference otherwise. Inasmuch as reference 51 obtained viscosity data for NO_2 and N_2O_4 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 N_2O 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_{ij} 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
$C_{int,1}$	term defined by eq. (24), dimensionless
$C_{rot,1}$	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_1	Sutherland constant for species 1, K
S_{1j}	Sutherland interaction constant for species 1 and j, K
T	temperature, K
x_1	mole fraction of species 1, dimensionless
Z_{rot}	rotational collision number
ϵ_1	depth of potential energy well for species 1, J
ϵ_{1j}	quantity defined by eq. (12)
η	viscosity, kg/m sec
η_1	viscosity of species 1, kg/m sec
η_{1j}	quantity defined by eqs. (10a) and (15), kg/m sec
λ	thermal conductivity, W/m K
λ_1	thermal conductivity for species 1, W/m K
λ_{1j}	quantity in table II, W/m K
σ_1	molecular diameter for species 1, A
σ_{1j}	quantity defined in eq. (11), A
φ_{1j}	viscosity interaction coefficient (eq. (6) or (8)), dimensionless
ψ_{1j}	frozen-thermal-conductivity interaction coefficient (eq. (2) and table II), dimensionless
$\Omega_{ij}^{(2,2)*}$	collision integral, dimensionless

Ω_{ij} collision cross section defined in eq. (14), \AA^2

Subscripts:

fr frozen contribution
i,j index for species
int internal contribution
mix for the mixture
react chemical reaction contribution
rot rotational contribution
tr translational contribution

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TABLE I. - EXPRESSIONS FOR φ_{ij} FOR MIXTURE VISCOSITY

Reference	Original expression for φ_{ij} given in reference	Exponent r in $\varphi_{ij} = k_{ij} m_{ij}^r$ (eq. (4))	
		For $k_{ij} =$	For $k_{ij} =$
Wilke, ref. 11	$\frac{1}{4} \left[1 + \left(\frac{\eta_j}{\eta_i} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 m_{ij}^{1/2}$	$\frac{\eta_j}{\eta_{ij}}$ (eq. (7))	$\frac{1}{4} \left[1 + \left(\frac{\eta_j}{\eta_i} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2$ (eq. (9))
Brokaw, ref. 12	$\frac{D_i A_{ij}^*}{D_{ij} A_i^*} = \frac{\lambda_j}{\lambda_{ij}} = \frac{\eta_j}{\eta_{ij}} m_{ij}$	1	1/2
Brokaw, ref. 12	$\frac{\lambda_j}{\lambda_{ij}} m_{ij}^{-1/8}$	7/8	3/8
Francis, ref. 13	$\frac{\bar{\omega}_{ij}}{\bar{\omega}_i} m_{ij}^{1/3}$	5/6	1/3
Sutherland, ref. 7	$\frac{\bar{\omega}_{ij}}{\bar{\omega}_j} m_{ij}^{1/4}$	3/4	1/4

TABLE II. - EXPRESSIONS FOR ψ_{ij} FOR MIXTURE FROZEN THERMAL CONDUCTIVITY

Reference	ψ_{ij}
Lindsay and Bromley, ref. 15	$\frac{1}{4} \left\{ 1 + \left[\frac{n_i}{n_j} \left(\frac{M_j}{M_i} \right)^{3/4} \frac{1 + \frac{S_i}{T}}{1 + \frac{S_j}{T}} \right]^2 \frac{1 + \frac{S_{ij}}{T}}{1 + \frac{S_i}{T}} \right\}$
Brokaw, ref. 12	$\varphi_{ij} \left[1 + \left(\frac{M_i - M_j}{M_i + M_j} \right)^2 \left(\frac{15}{4A_{ij}^*} - 1 \right) \left(1 + \frac{12B_{ij}^* + 5}{30 - 8A_{ij}^*} \frac{M_j}{M_i - M_j} \right) \right]$
Brokaw, ref. 12	$\varphi_{ij} \left[1 + \frac{2.54(M_i - M_j)(M_i - 0.177 M_j)}{(M_i + M_j)^2} \right]$
Brokaw, ref. 16	$\varphi_{ij} \left[1 + \frac{2.41(M_i - M_j)(M_i - 0.142 M_j)}{(M_i + M_j)^2} \right]$
Mason and Saxena, ref. 17	$1.065 \left\{ \frac{1}{4} m_{ij}^{1/2} \left[1 + \left(\frac{\lambda_i}{\lambda_j} \right)^{1/2} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2 \right\}$
Vanderslice et al., ref. 18	$\frac{1}{4} m_{ij}^{1/2} \left[1 + \left(\frac{\lambda_i}{\lambda_j} \right)^{1/2} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2$
Tondor and Saxena, ref. 19	$0.866 \left\{ \frac{1}{4} m_{ij}^{1/2} \left[1 + \left(\frac{\lambda_i}{\lambda_j} \right)^{1/2} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2 \right\}$

TABLE III. - AVERAGE ABSOLUTE PERCENT ERROR FOR Ar-NH₃

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

Method of calculation	Average absolute percent error		
	$\eta_{ij} = 148.2$ (eq. (15))	$\eta_{ij} = 164.8$ (eq. (10a))	$\eta_{ij} = 175.0$ (derived from experimental data)
Hirschfelder "rigorous" (ref. 3)	8.1	4.4	2.3
Wilke ^a (ref. 11)	5.8	5.8	5.8
Brokaw ($r = 1$) (ref. 12)	5.8	1.9	0.2
Brokaw ($r = 7/8$) (ref. 12)	6.9	3.1	1.0
Francis (ref. 13)	7.3	3.4	1.4
Sutherland (ref. 7)	8.0	4.2	2.2
Burgoyne ^a (ref. 20)	12.5	12.5	12.5

^aMethod does not use η_{ij} .

TABLE IV. - INPUT/OUTPUT DATA FILES

I/O unit	Data file
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

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

^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).

