

## Transport Properties of Burned Gas Mixture

*By*

Taeko SANO

*Summary:* The transport properties of viscosity coefficient, thermal conductivity and multidiffusion coefficient of the burned gas mixtures of *n*-octane by air are calculated by the approximate equations to the kinetic theory equations for the multicomponent gas mixtures. By using the values of collision diameter of molecular species obtained from the experimental data of viscosity of molecular species and expressed as a function of temperature, the transport properties of molecular species are calculated on the basis of the rigid-sphere potential in the molecular kinetic theory to be in good agreement with the experimental data. Although the accuracy of the calculated values of atomic and radical species can not be verified, the transport properties of burned gas mixtures are not misled by their unreliable values because of small mole fractions of atomic and radical species.

### 1. INTRODUCTION

The conditions of the wall along the path of burned gas flows have influences on the emission of air pollutants such as nitric oxide and carbon monoxide from combustion systems, on the heat transfer between burned gas flows and the wall in combustors and further on many phenomena subjected to burned gas flows in combustors.

In order to investigate theoretically the influence of the wall conditions on the flows of burned gas mixtures, the knowledge of transport properties of burned gas mixtures such as viscosity coefficient, thermal conductivity and diffusion coefficient controls definitely the phenomena as well as that of reaction mechanisms of burned gas mixtures does. However, the transport properties of burned gas mixtures are not available for the required range of composition and temperature at present.

The transport properties of multicomponent gas mixtures can be explained in terms of the kinetic theory using the distribution function of mixtures [1]. The distribution functions of molecules in mixtures are obtained by solving the Boltzmann equation which is a function of the intermolecular potential energy for each pair of species. The expressions for the transport fluxes in terms of the distribution function are hardly affected by the fact that chemical reactions are taking place in gaseous mixtures. Of the burned gas mixtures from hydrocarbon-air combustion systems, the transport phenomena can be thus explained satisfactorily by use of the distribution functions calculated from the first approximate solution to the Boltzmann equation.

The most used potential energy function for non-polar molecules at low temperature is the Lennard-Jones (6-12) potential and for polar molecules, the Stockmayer potential. However, it takes too much time to calculate the transport properties of gas mixtures based on the Lennard-Jones (6-12) and Stockmayer potentials.

In the present study, the transport properties were calculated based on the rigid-sphere potential. The burned gas mixtures of *n*-octane by air are considered and eleven species, CO, CO<sub>2</sub>, H, H<sub>2</sub>, H<sub>2</sub>O, N, N<sub>2</sub>, NO, O, O<sub>2</sub> and OH are taken into account as combustion products.

## 2. SYMBOLS

$C_p$	heat capacity at constant pressure
$C_v, \tilde{C}_v$	heat capacity at constant volume
$D_{ij}$	multicomponent diffusion coefficient of species <i>i</i> for species <i>j</i>
$\mathcal{D}_{ij}$	binary diffusion coefficient of species <i>i</i> for species <i>j</i>
$D^T$	thermal diffusion coefficient
$k$	Boltzmann constant
$M$	molecular weight
$m$	mass
$N$	mole fraction
$n$	number of particles per unit volume
$p$	pressure
$R$	gas constant
$T$	temperature
$\lambda$	thermal conductivity
$\mu$	viscosity coefficient
$\rho$	density
$\sigma$	collision diameter
$\sigma_{ij}$	collision diameter for binary collision of species <i>i</i> and <i>j</i>
Subscript	
$i$	species <i>i</i>

## 3. VISCOSITY COEFFICIENT

By using the distribution functions obtained by the first approximate solution to the Boltzmann equation, the viscosity coefficient  $\mu$  for multicomponent gas mixtures is given by

$$\mu = \frac{1}{2} kT \sum_{j=1}^{\nu} n_j b_{j0} \quad (1)$$

where  $b_{j0}$  is determined by the Boltzmann equation as ratios of two determinants of order  $\nu$ ,  $k$  the Boltzmann constant and  $n_j$  the number of particles per unit volume for species *j*. For the convenience of numerical computation, the above expression of the viscosity coefficient  $\mu$  can be written as

$$\mu = \frac{\begin{vmatrix} H_{11} & H_{12} \cdots H_{1\nu} & N_1 \\ H_{12} & & \\ \vdots & \vdots & \vdots \\ H_{1\nu} & & H_{\nu\nu} & N_\nu \\ N_1 & \cdots & N_\nu & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & H_{12} \cdots & H_{1\nu} \\ H_{12} & \cdots & \\ \vdots & & \vdots \\ H_{1\nu} & \cdots & H_{\nu\nu} \end{vmatrix}}, \quad (2)$$

where the elements  $H_{ij}$  are given in the form

$$\left. \begin{aligned} H_{ii} &= \frac{N_i^2}{\mu_i} + \sum_{\substack{k=1 \\ k \neq i}}^{\nu} \frac{2N_i N_k}{M_i + M_k} \frac{RT}{p \mathcal{D}_{ik}} \left( 1 + \frac{3}{5} \frac{M_k}{M_i} A_{ik}^* \right), \\ H_{ij} &= -\frac{2N_i N_j}{M_i + M_j} \frac{RT}{p \mathcal{D}_{ij}} \left( 1 - \frac{3}{5} A_{ij}^* \right) \quad (i \neq j), \end{aligned} \right\} \quad (3)$$

and binary diffusion coefficient  $\mathcal{D}_{ij}$  is expressed as

$$\mathcal{D}_{ij} = 0.0026280 \frac{\sqrt{T^3(M_i + M_j)/2M_i M_j}}{p \sigma_{ij}^2}, \quad (4)$$

where  $T$  is the temperature,  $p$  the pressure,  $R$  the universal gas constant ( $R = 82.055 \text{ cm}^3 \text{ atm/mol} \cdot \text{ }^\circ\text{K}$ ),  $M_i$  the molecular weight of species  $i$ ,  $N_i$  the mole fraction of species  $i$ ,  $\mu_i$  the viscosity coefficient of species  $i$ ,  $A_{ik}^*$  the dimensionless quantities which appear in the expressions for the transport coefficient of mixtures and given in terms of  $\Omega_{ij}^{(l,s)*}$ , the transformed collision integral ( $A_{ij}^* = \Omega_{ij}^{(2,2)*} / \Omega_{ij}^{(1,1)*}$  and are nearly unity) and  $\sigma_{ij}$  the collision diameter for binary collision of species  $i$  and  $j$ . The collision diameters  $\sigma_{ij}$  are obtained from the empirical combining laws,

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad (5)$$

where  $\sigma_i$  and  $\sigma_j$  are collision diameters of species  $i$  and  $j$ , respectively.

Even though Eq. (2) is written in the form of computational purpose, it is very complex and takes much computational time to calculate the viscosity coefficient of multicomponent gas mixtures, so a more tractable equation to obtain the viscosity coefficient  $\mu$  has been asked. For such an equation, we examined the following equation (6) satisfactorily to approximate the kinetic theory equation (2)

$$\mu = \sum_{i=1}^{\nu} \frac{N_i^2}{N_i^2 / \mu_i + 1.385 \sum_{\substack{k=1 \\ k \neq i}}^{\nu} N_i N_k RT / p M_i \mathcal{D}_{ik}}, \quad (6)$$

where  $R = 82.055 \text{ cm}^3 \text{ atm/mol} \cdot \text{ }^\circ\text{K}$ .

In order to calculate the viscosity coefficient of multicomponent gas mixtures by Eq. (6), we must know the viscosity coefficients  $\mu_i$  for all species. In literatures, for all species, we do not have complete knowledge of the viscosity coefficient and, even though we found the experimental data, they were valid only for temperature below 1500°K.

On the other hand, the molecular kinetic theory predicts the viscosity coefficient  $\mu_i$  with the collision diameter  $\sigma_i$  as

$$\mu_i = 266.93 \times 10^{-7} \sqrt{M_i T} / \sigma_i^2. \quad (7)$$

If we know the collision diameter of species in any way, the viscosity coefficient can be estimated by this relation.

The values of collision diameter  $\sigma_i^D$  based on the Lennard-Jones (6-12) potential for molecular species CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, NO and O<sub>2</sub> are available from the monograph by Hirschfelder et al [1]. Using these collision diameter  $\sigma_i^D$  based on the Lennard-Jones (6-12) potential, we can calculate their viscosity coefficients  $\mu_i$  by Eq. (7) based on the rigid-sphere potential, which do not agree with the experimental data in references [1], [2]. To improve the inconsistency of the used type of potential, the values of collision diameter  $\sigma_i$  for these species have to be calcula-

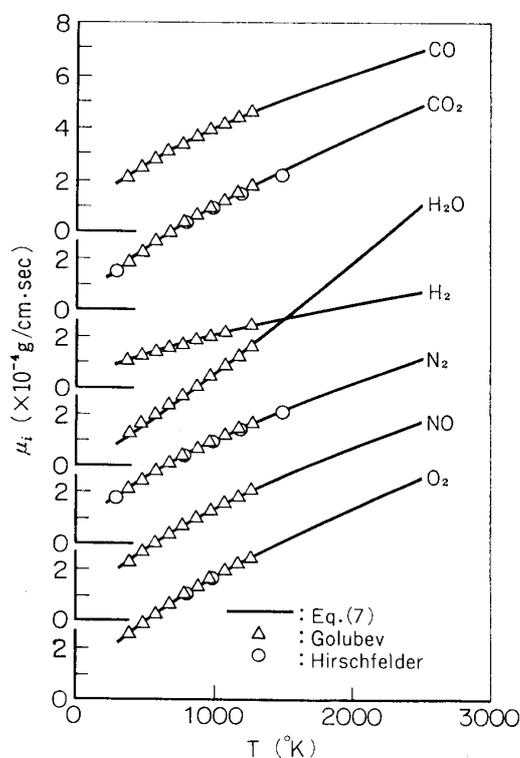


FIG. 1. Comparison of the calculated and the experimental values of viscosity of molecular species.

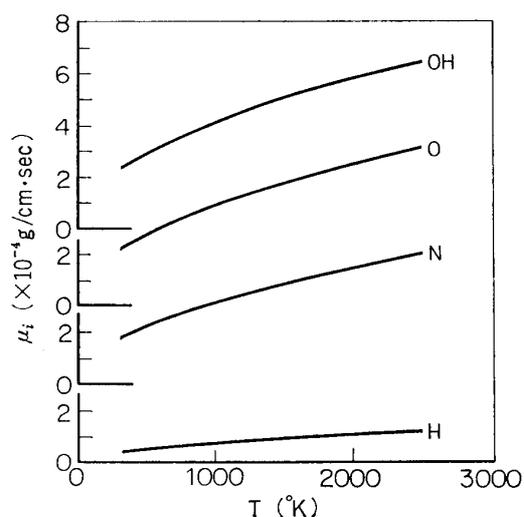


FIG. 2. Calculated values of viscosity of atomic and radical species.

TABLE 1. Values of Collision Diameter  $\sigma_i^D(T)$  Å.  
 $\sigma_i^D(T) = A \cdot T^{-B}$

Species $i$	A	B
CO	5.11	0.06
CO <sub>2</sub>	8.95	0.12
H	3.39	0.00
H <sub>2</sub>	4.25	0.08
H <sub>2</sub> O	30.1	0.33
N	3.16	0.00
N <sub>2</sub>	5.43	0.07
NO	5.12	0.065
O	2.96	0.00
O <sub>2</sub>	5.34	0.075
OH	2.92	0.00

TABLE 2. Comparison of Viscosity Coefficient by Kinetic Equation and Approximate Equation for Burned Gas Mixtures\*)

A/F	T°K	$\mu$ ( $\times 10^{-4}$ g/cm·sec)	
		Eq. (2)	Eq. (6)
8	1835	5.5	5.6
10	2103	6.1	6.2
12	2297	6.6	6.6
14	2402	6.9	6.9
15	2392	6.9	6.9
16	2350	6.8	6.9
18	2229	6.5	6.7

\*) *n*-Octane burns with air adiabatically and the produced combustion gas mixtures are in equilibrium at the adiabatic combustion temperature  $T$  determined by air-fuel ratio (A/F), pressure  $p$  and initial temperature  $T_0$  ( $T_0 = 298^\circ\text{K}$  and  $p = 5$  atm).

ted by Eq. (7) using the experimental data of viscosity  $\mu_i$  for temperature ranging from  $300^\circ\text{K}$  to  $1273^\circ\text{K}$ . The obtained collision diameters  $\sigma_i^D(T)$  are then expressed as a function of temperature  $T$ . With these collision diameters, we can calculate the viscosity coefficients  $\mu_i$  of those species for temperature ranging extrapolated from  $300^\circ\text{K}$  to  $2500^\circ\text{K}$  by Eq. (7). In Fig. 1, the calculated values of viscosity coefficient by Eq. (7) are plotted for temperature  $T$  to be compared with the experimental data. It is shown that good agreement exists between the experimental data of viscosity and the calculated results.

For atomic species H, N and O, we could not find their experimental data of viscosity in references, so utilized the values of collision diameter from the reference [3]. For radical species OH, both the experimental data of viscosity and the

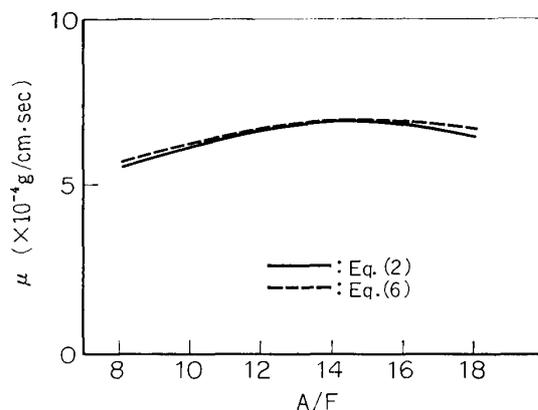


FIG. 3. Comparison of viscosity coefficient by kinetic equation and approximate equation of burned gas mixtures.

value of collision diameter have not been obtained in references, hence, the value of collision diameter of species OH was determined by an empirical equation using atomic volume [4]. The calculated values of viscosity coefficient  $\mu_i$  for species H, N, O and OH are shown (in Fig. 2).

Though the accuracy of the calculated values of viscosity coefficient  $\mu_i$  for species H, N, O and OH is left to be examined in the future work, they are sufficiently enough approximate values for the present work. Because, according to Eq. (6), the viscosity coefficient  $\mu$  of multicomponent gas mixtures depends on the mole fraction of species  $i$  in gas mixtures. In the reacting gas mixtures which we are concerned with, the mole fraction of species  $N_2$  is more than 0.7 and the sum of the mole fraction of atomic and radical species is less than 0.1. Therefore, the viscosity coefficient of the gas mixtures for the present work is almost determined by the viscosity coefficient of molecular species, and in a certain case, only by the viscosity coefficient of species  $N_2$ .

The values of collision diameter  $\sigma_i^D(T)$  used for the present work are summarized in Table 1. A comparison of the results obtained from the kinetic equation (2) with the approximate equation (6) is made in Table 2 and Fig. 3 for the burned gas mixtures produced by the adiabatic combustion of  $n$ -octane and air. It is shown that Eq. (6) approximates Eq. (2) fairly well and can be used as a tractable equation for the prediction of the viscosity coefficient of burned gas mixtures.

#### 4. THERMAL CONDUCTIVITY

By using the distribution functions obtained from the first approximate solution to the Boltzmann equation, the coefficient of thermal conductivity  $\lambda$  for multicomponent gas mixtures is expressed as [1]

$$\lambda = \lambda' - \frac{k}{2n} \sum_{i=1}^{\nu} \sum_{\substack{j=1 \\ j \neq i}}^{\nu} \frac{n_i n_j}{\mathcal{D}_{ij}} \left( \frac{D_i^T}{n_i m_i} - \frac{D_j^T}{n_j m_j} \right)^2, \quad (8)$$

where the quantity  $\lambda'$  is given by the following equation

$$\lambda' = -\frac{75}{8} k^2 T \frac{\begin{vmatrix} q_{11}^{00} \cdots q_{1\nu}^{00} & q_{11}^{01} \cdots q_{1\nu}^{01} & 0 \\ \vdots & \vdots & \vdots \\ q_{\nu 1}^{00} \cdots q_{\nu\nu}^{00} & q_{\nu 1}^{01} \cdots q_{\nu\nu}^{01} & 0 \\ q_{11}^{10} \cdots q_{1\nu}^{10} & q_{11}^{11} \cdots q_{1\nu}^{11} & 1 \\ \vdots & \vdots & \vdots \\ q_{\nu 1}^{10} \cdots q_{\nu\nu}^{10} & q_{\nu 1}^{11} \cdots q_{\nu\nu}^{11} & 1 \\ 0 \cdots 0 & 1 \cdots 1 & 0 \end{vmatrix}}{\begin{vmatrix} q_{11}^{00} \cdots q_{1\nu}^{00} & q_{11}^{01} \cdots q_{1\nu}^{01} \\ \vdots & \vdots \\ q_{\nu 1}^{00} \cdots q_{\nu\nu}^{00} & q_{\nu 1}^{01} \cdots q_{\nu\nu}^{01} \\ q_{11}^{10} \cdots q_{1\nu}^{10} & q_{11}^{11} \cdots q_{1\nu}^{11} \\ \vdots & \vdots \\ q_{\nu 1}^{10} \cdots q_{\nu\nu}^{10} & q_{\nu 1}^{11} \cdots q_{\nu\nu}^{11} \end{vmatrix}}, \quad (9)$$

where

$$q_{ij}^{mm'} = \frac{\sqrt{m_i m_j}}{n_i n_j} \tilde{Q}_{ij}^{mm'}, \quad (10)$$

and  $\tilde{Q}_{ij}^{mm'}$  are those given in terms of the transformed collision integral  $\Omega_{ij}^{(l,s)}$ , further  $k$  is the Boltzmann constant,  $n_i$  the number of particles per unit volume for species  $i$ ,  $m_i$  the mass of species  $i$ ,  $n$  the number of particles per unit volume,  $\mathcal{D}_{ij}$  the binary diffusion coefficient and  $D_i^T$  the thermal diffusion coefficient of species  $i$ .

For the convenience of numerical computation, Eq. (8) can be rewritten in the form

$$\lambda = \lambda' - \frac{1}{2} R \sum_{i=1}^{\nu} \sum_{\substack{j=1 \\ j \neq i}}^{\nu} \frac{RTN_i N_j}{p \mathcal{D}_{ij}} \left( \frac{D_i^T}{N_i M_i} - \frac{D_j^T}{N_j M_j} \right)^2, \quad (11)$$

where  $R$  is the universal gas constant,  $N_i$  the mole fraction of species  $i$  and  $M_i$  the molecular weight of species  $i$ , with a much simpler expression of  $\lambda'$ ,

$$\lambda' = 4 \frac{\begin{vmatrix} L_{11}^{11} \cdots L_{1\nu}^{11} & N_1 \\ \vdots & \vdots \\ L_{\nu 1}^{11} \cdots L_{\nu\nu}^{11} & N_\nu \\ N_1 \cdots N_\nu & 0 \end{vmatrix}}{\begin{vmatrix} L_{11}^{11} \cdots L_{11}^{11} \\ \vdots \\ L_{\nu 1}^{11} \cdots L_{\nu\nu}^{11} \end{vmatrix}}, \quad (12)$$

where the elements  $L_{ij}$  are given by Eq. (13)

$$\left. \begin{aligned} L_{ii}^{11} &= -\frac{4N_i^2}{\lambda_i} - \frac{16}{25} \frac{T}{p} \sum_{k \neq i}^{\nu} \frac{N_i N_k \left( \frac{15}{2} M_i^2 + \frac{25}{4} M_k^2 - 3M_k^2 B_{ik}^* + 4M_i M_k A_{ik}^* \right)}{(M_i + M_k)^2 \mathcal{D}_{ik}} \\ L_{ij}^{11} &= \frac{16}{25} \frac{T}{p} \frac{N_i N_j M_i M_j}{(M_i + M_j)^2 \mathcal{D}_{ij}} \left( \frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right) \quad (i \neq j), \end{aligned} \right\} (13)$$

$A_{ij}^*$  and  $B_{ij}^*$  are given in terms of transformed collision integral  $\Omega_{ij}^{(l,s)*}$ ,

$$\begin{aligned} A_{ij}^* &= \Omega_{ij}^{(2,2)*} / \Omega_{ij}^{(1,1)*}, \\ B_{ij}^* &= \frac{5\Omega_{ij}^{(1,2)*} - 4\Omega_{ij}^{(1,3)*}}{\Omega_{ij}^{(1,1)*}}, \end{aligned}$$

and they are nearly unity.

Muckenfuss and Curtiss [5] proposed that the thermal conductivity coefficient  $\lambda$  of multicomponent gas mixtures can be given only by  $\lambda'$ . Truly, the second term of right-hand side in Eq. (11) is small to be neglected compared with the first term, because the second term means the difference between the diffusion ratio of species  $i$  and that of species  $j$  and the values of the diffusion ratio for burned gas mixtures are small as mentioned in Section 6. Here, we calculated the thermal conductivity coefficient assuming that  $\lambda$  equals to  $\lambda'$  given by Eq. (12).

To calculate the thermal conductivity of burned gas mixtures, Eq. (12) takes much computation time. There have been several approximate equations proposed. Mason [6] proposed an approximate equation (14) as a result of simplification of Eq. (12)

$$\lambda = \sum_{i=1}^{\nu} \lambda_i \left( 1 + \sum_{\substack{k=1 \\ k \neq i}}^{\nu} G_{ik} \frac{N_k}{N_i} \right)^{-1}, \quad (14)$$

where

$$G_{ik} = \frac{1.065}{2\sqrt{2}} \left( 1 + \frac{M_i}{M_k} \right)^{-1} \left\{ 1 + \left( \frac{\lambda_i}{\lambda_k} \right)^{1/2} \left( \frac{M_i}{M_k} \right)^{1/4} \right\}^2,$$

and  $\lambda_i$  is the thermal conductivity of species  $i$ .

The thermal conductivity  $\lambda_i$  of species  $i$  is related with the viscosity coefficient  $\mu_i$  of species  $i$  in the molecular kinetic theory [1],

$$\lambda_i = \frac{15}{4} \frac{R}{M_i} \mu_i \left( \frac{4}{15} \frac{\tilde{C}_{vi}}{R} + \frac{3}{5} \right), \quad (15)$$

where  $\tilde{C}_{vi}$  is the molal heat capacity at constant volume of species  $i$  and  $R=1.98726$  cal/mol $\cdot$ °K. In Fig. 4, the calculated results of thermal conductivity  $\lambda_i$  for molecular species CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, NO and O<sub>2</sub> are plotted for temperature  $T$  compared with the experimental data [7] and for atomic and radical species H, N, O and OH are shown in Fig. 5.

A comparison of the results obtained from the kinetic equation (12) with the approximate equation (14) is presented in Table 3 and Fig. 6 for burned gas mixtures. It is shown that Eq. (14) sufficiently approximates (12), though the former overestimates the latter.

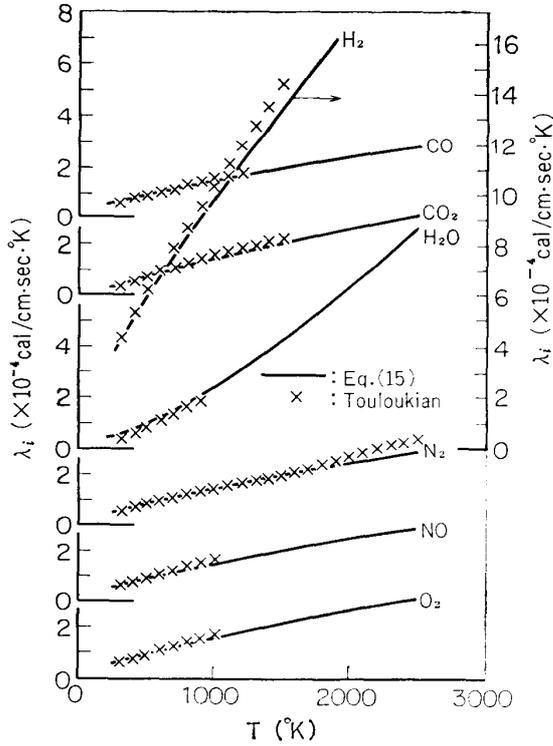


FIG. 4. Comparison of the calculated and the experimental values of thermal conductivity of molecular species.

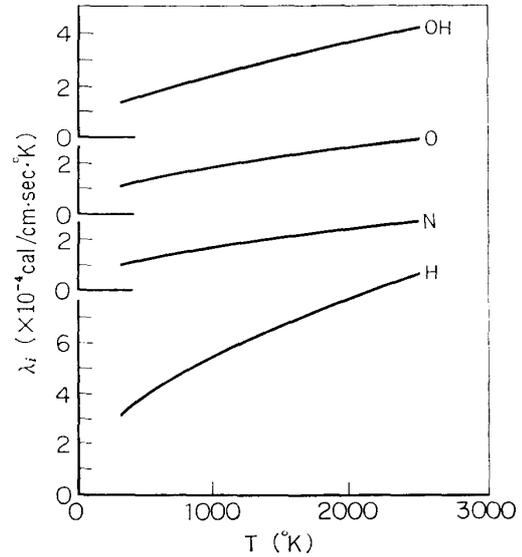


FIG. 5. Calculated values of thermal conductivity of atomic and radical species.

TABLE 3. Comparison of Thermal Conductivity by Kinetic Equation and Approximate Equation for Burned Gas Mixtures\*)

A/F	T°K	$\lambda (\times 10^{-4} \text{ cal/cm}\cdot\text{sec}\cdot^{\circ}\text{K})$	
		Eq. (12)	Eq. (14)
8	1835	4.2	5.3
10	2103	4.4	4.6
12	2297	4.4	4.1
14	2402	3.9	3.9
15	2392	3.5	3.7
16	2350	3.2	3.6
18	2229	2.8	3.3

\*) Combustion conditions are the same as those of the viscosity coefficient calculations.

### 5. DIFFUSION COEFFICIENT

The distribution function gives the multicomponent diffusion coefficient  $D_{ij}$  as

$$D_{ij} = \frac{\rho n_i}{2nm_j} \sqrt{\frac{2kT}{m_i}} C_{i_0}^{(j,i)}, \quad (16)$$

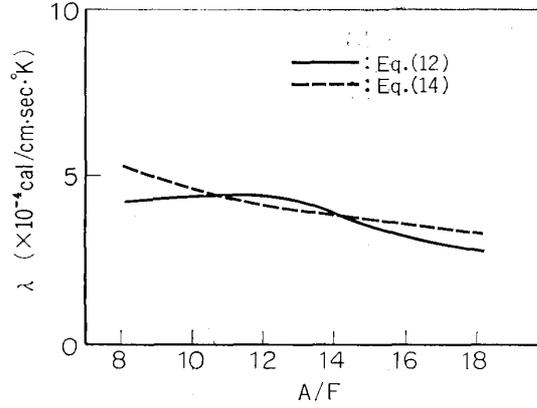


FIG. 6. Comparison of thermal conductivity by kinetic equation and approximate equation of burned gas mixtures.

where  $C_{i0}^{(j,i)}$  are the coefficient determined by solution of the Boltzmann equation,  $n$  the number of particles per unit volume and  $m_i$  the mass of particle for species  $i$ .

The first approximation [1] to the Boltzmann equation in multicomponent mixtures yields the following relation of the diffusion coefficient  $D_{ij}$

$$\sum_{j=1}^{\nu} F_{ij}(m_h D_{jh} - m_k D_{jk}) = (\delta_{ih} - \delta_{ik}), \quad (17)$$

where

$$F_{ij} = \left( \frac{n_i}{\rho \mathcal{D}_{ij}} + \sum_{l \neq i} \frac{n_l m_j}{\rho m_i \mathcal{D}_{il}} \right) (1 - \delta_{ij}), \quad (18)$$

and  $\mathcal{D}_{ij}$  is the binary diffusion coefficient obtained from Eq. (4) and tabulated in Table 4 to be compared with the experimental values [1]. Equation (17) gives an alternative expression of Eq. (16)

$$D_{ij} = \frac{F^{ji} - F^{ii}}{m_j |F|}, \quad (19)$$

where  $|F|$  is the determinant of the  $F_{ij}$  and the  $F^{ji}$  are the minors, or by replacing  $n_i$  in Eq. (18) by the mole fraction of species  $i$ ,  $N_i$

$$D_{ij} = \frac{1}{M_j} \left( \sum_{k=1}^{\nu} N_k M_k \right) \frac{K^{ji} - K^{ii}}{|K|}, \quad (20)$$

where  $K_{ii} = 0$

$$K_{ij} = \frac{N_i}{\mathcal{D}_{ij}} + \frac{M_j}{M_i} \sum_{k \neq i} \frac{N_k}{\mathcal{D}_{ik}} \quad i \neq j, \quad (21)$$

and  $|K|$  is the determinant of the  $K_{ij}$  and the  $K^{ji}$  are the minors.

It consumes much computational time to calculate the multidiffusion coefficient by Eq. (20) as well as in the calculation of the viscosity coefficient and the thermal

TABLE 4. Binary Diffusion Coefficient  $\mathcal{D}_{12}$  at 1 atm.

Gas pair	T°K	Calculated (cm <sup>2</sup> /sec)				Experimental $\mathcal{D}_{12}$
		Authors		Hirschfelder [1]		
		$\sigma_{12}^D(\text{Å})$	$\mathcal{D}_{12}$	$\sigma_{12}(\text{Å})$	$\mathcal{D}_{12}$	
N <sub>2</sub> -CO	273.2	3.66	0.168	3.636	0.174	0.192
	298.2	3.64	0.193			
N <sub>2</sub> -CO <sub>2</sub>	273.3	4.05	0.124	3.839	0.130	0.144
	298.2	4.02	0.143			
N <sub>2</sub> -H	298.2	3.52	0.784	3.325	0.656	0.674
N <sub>2</sub> -H <sub>2</sub>	273.2	3.19	0.602			
	298.2	3.17	0.695			
N <sub>2</sub> -H <sub>2</sub> O	298.2	4.19	0.165			
N <sub>2</sub> -N	298.2	3.40	0.270			
N <sub>2</sub> -N <sub>2</sub>	353.2	3.60	0.254		0.273	0.287
N <sub>2</sub> -NO	298.2	3.59	0.195			
N <sub>2</sub> -O	298.2	3.30	0.275			
N <sub>2</sub> -O <sub>2</sub>	273.2	3.59	0.169	3.557	0.175	0.181
	298.2	3.56	0.195			
N <sub>2</sub> -OH	298.2	3.27	0.275			

conductivity using the kinetic equations. However, there is found no approximate equation to the multidiffusion coefficient proposed.

When we try to investigate theoretically the influence of the wall conditions on the flow, it is practically impossible from the point of the computer ability in the present time to calculate the multidiffusion coefficient  $D_{ij}$  of burned gas mixtures with consideration for the changes in the temperature and composition of mixtures which are caused by the wall conditions.

The multidiffusion coefficient  $D_{ij}$  is affected by the mole fraction of species. In burned gas mixtures, the mole fraction  $N_i$  of such molecular species as N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>, whose sum is more than 0.8, does not almost change and the change in the mole fraction of atomic species, whose sum is less than 0.1, is relatively large. The multidiffusion coefficient of burned gas mixtures may be thus determined by the molecular species and weakly dependent upon the large changing mole fraction of atomic species.

In order to examine its dependence on the mole fraction of species, the multidiffusion coefficient was calculated by changing the concentration (mole per unit volume) of one component and keeping other concentration constant in the burned gas mixtures by oxidation of *n*-octane by air ( $A/F=15$ ).

Some examples of the calculation are shown in Figs. 7–11. In Figs. 7 and 8, the multidiffusion coefficient of species CO to species  $j$ ,  $D_{co,j}$  and that of species  $i$  to species CO,  $D_{i,co}$  are plotted for the mole fraction of species CO and they changed not so much by the change in the mole fraction of species CO. In the case of  $A/F=15$ , the equilibrium concentration of species CO in burned gas mixtures is small compared with that of species N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>.

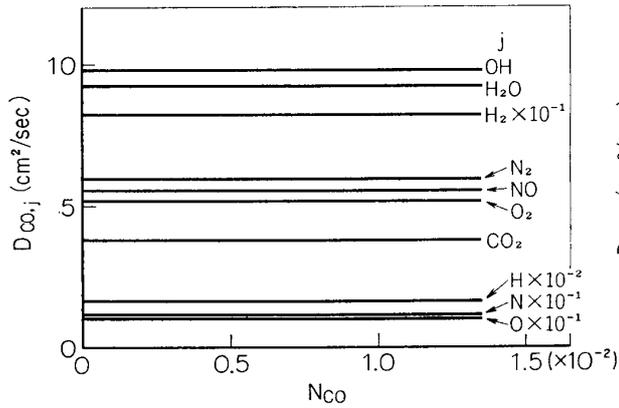


FIG. 7. Multidiffusion coefficient of species CO to species  $j$ .

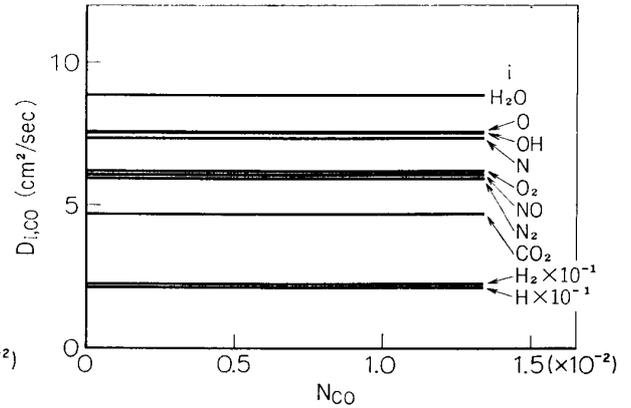


FIG. 8. Multidiffusion coefficient of species  $i$  to species CO.

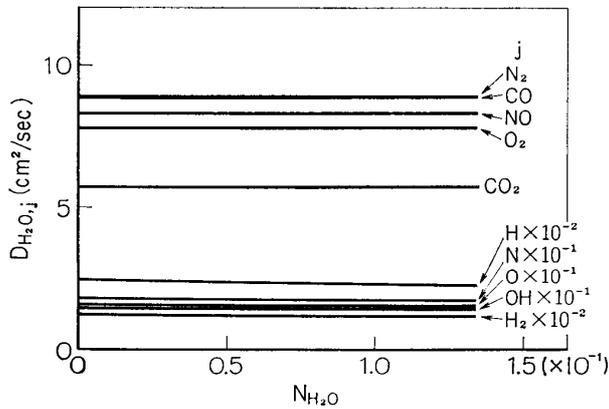


FIG. 9. Multidiffusion coefficient of species  $H_2O$  to species  $j$ .

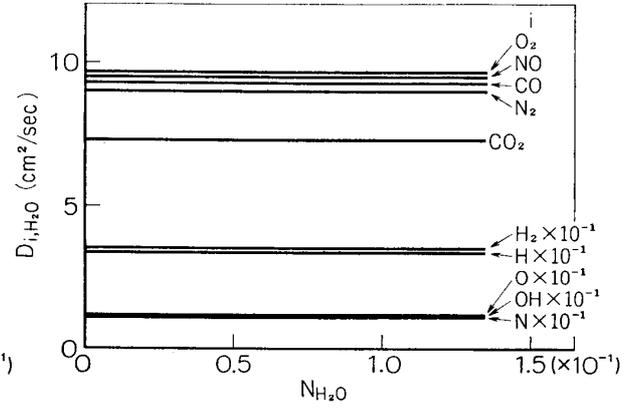


FIG. 10. Multidiffusion coefficient of species  $i$  to species  $H_2O$ .

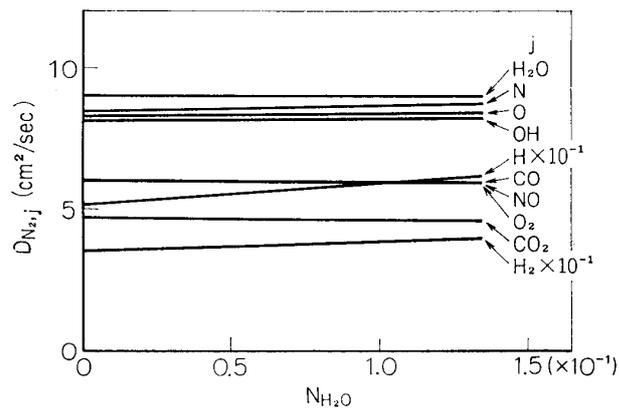


FIG. 11. Multidiffusion coefficient of species  $N_2$  to species  $j$ .

The change in the mole fraction of species H, N, O and OH by the temperature change is larger than that of species CO in the present burned gas mixtures. However, the absolute values of the concentration of those species are small compared with those of species  $N_2$ ,  $H_2O$  and  $CO_2$ , so the values of  $D_{ij}$  are little

affected by the change in the mole fraction of those species as well as by the change in the mole fraction of species CO. In other words, the mole fraction of species  $N_2$ ,  $H_2O$  and  $CO_2$  which occupy more than 80% in burned gas mixtures is not influenced by the change in the mole fraction of atomic and radical species such as H, N, O and OH, and the values of  $D_{ij}$  are determined by the mole fraction of molecular species in large quantities.

The equilibrium concentration of species  $H_2O$  in the burned gas mixtures at  $A/F=15$  and  $p=5$  atm is about 13% in volume percent and the largest concentration next to species  $N_2$ . If the concentration of species  $H_2O$  changes from its equilibrium concentration to zero, the mole fraction of all species changes in a considerable magnitude. In Figs. 9 and 10, the values of the multidiffusion coefficient of species  $H_2O$  to species  $j$ ,  $D_{H_2O,j}$  and that of species  $i$  to  $H_2O$ ,  $D_{i,H_2O}$  are calculated for the mole fraction of species  $H_2O$  changed from its equilibrium to zero. As it is clear from the figures, the values of  $D_{H_2O,j}$  and  $D_{i,H_2O}$  are almost constant. In Fig. 11, the values of the multidiffusion coefficient of species  $N_2$  to species  $j$ ,  $D_{N_2,j}$  whose dependence on the change in the mole fraction of species  $H_2O$  is relatively large, are presented for the mole fraction  $N_{H_2O}$ .

From these calculated results, it can be concluded that the values of  $D_{ij}$  are mainly determined by molecular species and are nearly constant within the change in the mole fraction of atomic and radical species, and it is not necessary to consider the change of mole fraction in the calculation of  $D_{ij}$ , but only the change of temperature must be taken into account.

## 6. THERMAL DIFFUSION COEFFICIENT

The distribution function gives the multicomponent thermal diffusion coefficient  $D_i^T$  as [1]

$$D_i^T = \frac{n_i m_i}{2} \sqrt{\frac{2kT}{m_i}} a_{i0}, \quad (22)$$

where  $a_{i0}$  is the coefficient determined by solution of the Boltzmann equation.

By taking the second terms in approximate equation to the Boltzmann equation in multicomponent mixtures, the following relation of the thermal diffusion coefficient  $D_i^T$  is given

$$D_i^T = -\frac{8M_i}{5R} \left( \begin{array}{cccc|cccc} L_{11}^{00} & \cdots & L_{1\nu}^{00} & L_{11}^{01} & \cdots & L_{1\nu}^{01} & 0 & \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & \\ L_{\nu 1}^{00} & \cdots & L_{\nu\nu}^{00} & L_{\nu 1}^{01} & \cdots & L_{\nu\nu}^{01} & 0 & \\ L_{11}^{10} & \cdots & L_{1\nu}^{10} & L_{11}^{11} & \cdots & L_{1\nu}^{11} & N_1 & \\ \vdots & & \vdots & \vdots & & \vdots & \vdots & \\ L_{\nu 1}^{10} & \cdots & L_{\nu\nu}^{10} & L_{\nu 1}^{11} & \cdots & L_{\nu\nu}^{11} & N_\nu & \\ N_1 \delta_{1i} & \cdots & N_\nu \delta_{\nu i} & 0 & \cdots & 0 & 0 & \end{array} \right) \left( \begin{array}{cccc} L_{11}^{00} & \cdots & L_{1\nu}^{00} & L_{11}^{01} & \cdots & L_{1\nu}^{01} \\ \vdots & & \vdots & \vdots & & \vdots \\ L_{\nu 1}^{00} & \cdots & L_{\nu\nu}^{00} & L_{\nu 1}^{01} & \cdots & L_{\nu\nu}^{01} \\ L_{11}^{10} & \cdots & L_{1\nu}^{10} & L_{11}^{11} & \cdots & L_{1\nu}^{11} \\ \vdots & & \vdots & \vdots & & \vdots \\ L_{\nu 1}^{10} & \cdots & L_{\nu\nu}^{10} & L_{\nu 1}^{11} & \cdots & L_{\nu\nu}^{11} \end{array} \right) \quad (23)$$

where

$$\begin{aligned}
L_{ii}^{00} &= 0, \\
L_{ij}^{00} &= \frac{16T}{25p} \left[ \frac{N_i N_j}{\mathcal{D}_{ij}} + \sum_{k \neq i} \frac{N_j N_k M_j}{M_i \mathcal{D}_{ik}} \right] \quad i \neq j, \\
L_{ii}^{01} &= \frac{8T}{5p} \sum_{k \neq i} \frac{N_i N_k M_k \left( \frac{6}{5} C_{ik}^* - 1 \right)}{(M_i + M_k) \mathcal{D}_{ik}}, \\
L_{ij}^{01} &= -\frac{8T}{5p} N_i N_j \frac{M_i \left( \frac{6}{5} C_{ij}^* - 1 \right)}{(M_i + M_j) \mathcal{D}_{ij}} \quad i \neq j, \\
L_{ij}^{10} &= \frac{M_j}{M_i} L_{ij}^{01}, \\
L_{ii}^{11} &= -\frac{4N_i^2}{\lambda_i} - \frac{16}{25} \frac{T}{p} \sum_{k \neq i} \frac{N_i N_k \left( \frac{15}{2} M_i^2 + \frac{25}{4} M_k^2 - 3M_k^2 B_{ik}^* + 4M_i M_k A_{ik}^* \right)}{(M_i + M_k) \mathcal{D}_{ik}}, \\
L_{ij}^{11} &= \frac{16T}{25p} \frac{N_i N_j M_i M_j}{(M_i + M_j)^2 \mathcal{D}_{ij}} \left[ \frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right] \quad i \neq j.
\end{aligned} \tag{24}$$

It is very troublesome to calculate the thermal diffusion coefficient  $D_i^T$  by Eq. (23). If the term by the thermal diffusion is negligible small compared with that by the ordinary diffusion, the necessity of the calculation of the thermal diffusion coefficient is thus obviated.

If  $K_T$  is defined by the following equation for two component systems of species  $i$  and  $j$

$$K_T = \frac{\rho}{n^2 m_i m_j} \frac{\mathcal{D}_i^T}{\mathcal{D}_{ij}}, \tag{25}$$

where  $\mathcal{D}_{ij}$  is the binary diffusion coefficient of species  $i$  for species  $j$ ,  $\rho$  the density,  $n$  the number of particles per unit volume and  $m_i$  the mass per particle, the defined value means a measure of the relative importance of the thermal and ordinary diffusion.  $K_T$  is then given by the following equation

$$K_T = \frac{N_i N_j}{6\lambda_{ij}} \frac{S^{(i)} N_i - S^{(j)} N_j}{X_\lambda + Y_\lambda} (6C_{ij}^* - 5), \tag{26}$$

where

$$\begin{aligned}
S^{(i)} &= \frac{M_i + M_j}{2M_j} \frac{\lambda_{ij}}{\lambda_i} - \frac{15}{4A_{ij}^*} \left( \frac{M_j - M_i}{2M_i} \right) - 1, \\
S^{(j)} &= \frac{M_j + M_i}{2M_i} \frac{\lambda_{ij}}{\lambda_j} - \frac{15}{4A_{ij}^*} \left( \frac{M_i - M_j}{2M_j} \right) - 1, \\
X_\lambda &= \frac{N_i^2}{\lambda_i} + \frac{2N_i N_j}{\lambda_{ij}} + \frac{N_j^2}{\lambda_j},
\end{aligned}$$

$$\begin{aligned}
 Y_\lambda &= \frac{N_i^2}{\lambda_i} U^{(i)} + \frac{2N_i N_j}{\lambda_{ij}} U^{(x)} + \frac{N_j^2}{\lambda_j} U^{(j)}, \\
 U^{(i)} &= \frac{4}{15} A_{ij}^* - \frac{1}{12} \left( \frac{12}{5} B_{ij}^* + 1 \right) \frac{M_i}{M_j} + \frac{1}{2} \frac{(M_i - M_j)^2}{M_i M_j}, \\
 U^{(j)} &= \frac{4}{15} A_{ij}^* - \frac{1}{12} \left( \frac{12}{5} B_{ij}^* + 1 \right) \frac{M_j}{M_i} + \frac{1}{2} \frac{(M_j - M_i)^2}{M_i M_j}, \\
 U^{(x)} &= \frac{4}{15} A_{ij}^* \left\{ \frac{(M_i + M_j)^2}{4M_i M_j} \right\} \frac{\lambda_{ij}^2}{\lambda_i \lambda_j} - \frac{1}{12} \left( \frac{12}{5} B_{ij}^* + 1 \right) \\
 &\quad - \frac{5}{32A_{ij}^*} \left( \frac{12}{5} B_{ij}^* - 5 \right) \frac{(M_i - M_j)^2}{M_i M_j},
 \end{aligned} \tag{27}$$

where  $\lambda_i$  is the thermal conductivity of species  $i$ ,  $\lambda_{ij}$  the thermal conductivity for two component systems of species  $i$  and  $j$ . The quantity  $K_T$  is so defined that when  $K_T > 0$ , species  $i$  moves to the cold region, and when  $K_T < 0$ , species  $i$  moves to the hot region.

If it is assumed that burned gas mixtures consist of the two component systems of each species in multicomponent gas mixtures and nitrogen whose concentration is more than 70% of the burned gas mixtures for the present work, the diffusion ratio  $K_T$  for those two component systems can be easily calculated by Eq. (26). As a example of the calculation, the values of diffusion ratio  $K_T$  of species  $i$  for nitrogen in burned gas mixtures at  $A/F=15$  are listed in Table 5. Evidently, the thermal diffusion coefficient is of no significance compared with the ordinary diffusion.

TABLE 5. Values of Diffusion Ratio  $K_T$  of Species  $i$  for Nitrogen in Burned Gas Mixtures\*)

Species $i$	$K_T$
CO	$-1.8 \times 10^{-3}$
CO <sub>2</sub>	$-3.3 \times 10^{-3}$
H	$-1.3 \times 10^{-4}$
H <sub>2</sub>	$-1.1 \times 10^{-3}$
H <sub>2</sub> O	$-1.2 \times 10^{-2}$
N	$-9.4 \times 10^{-9}$
NO	$-5.1 \times 10^{-4}$
O	$-5.4 \times 10^{-5}$
O <sub>2</sub>	$-8.1 \times 10^{-4}$
OH	$-8.7 \times 10^{-4}$

\*) Combustion conditions are the same as those of the viscosity coefficient calculation.

## 7. TRANSPORT PROPERTIES OF BURNED GAS MIXTURES

By using the approximate equations (6) and (14) for viscosity coefficient  $\mu$  and thermal conductivity  $\lambda$  of the multicomponent gas mixtures, respectively, the viscosity

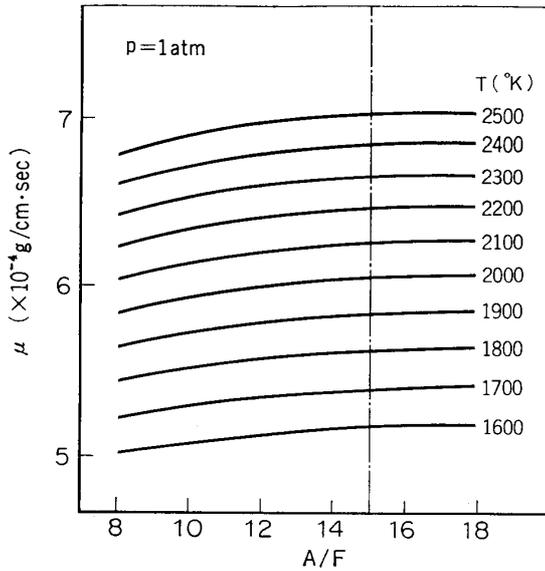


FIG. 12. Viscosity coefficient of burned gas mixtures.

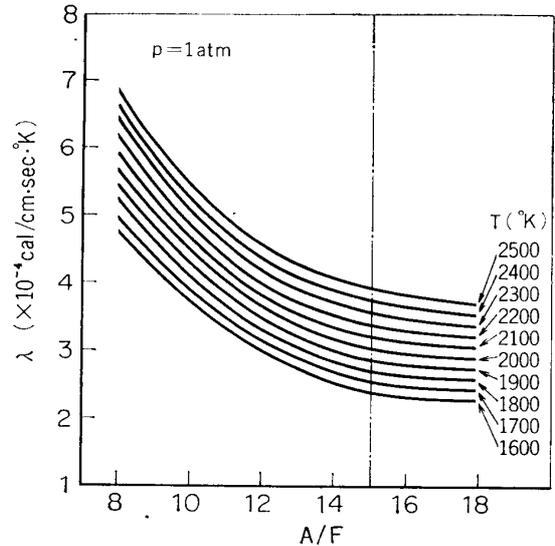


FIG. 13. Thermal conductivity of burned gas mixtures.

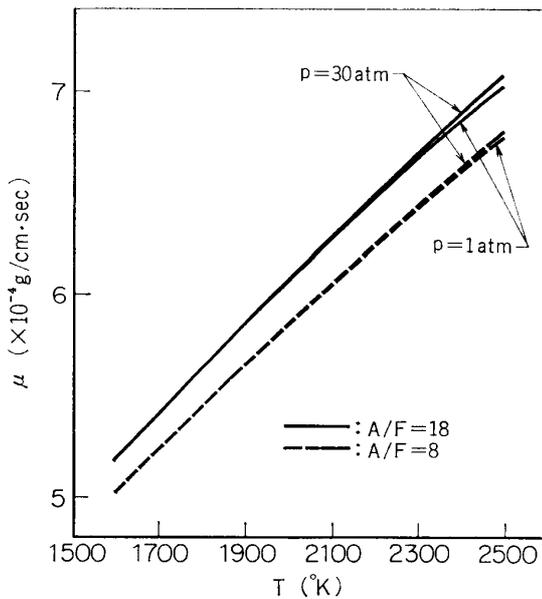


FIG. 14. Viscosity coefficient of burned gas mixtures.

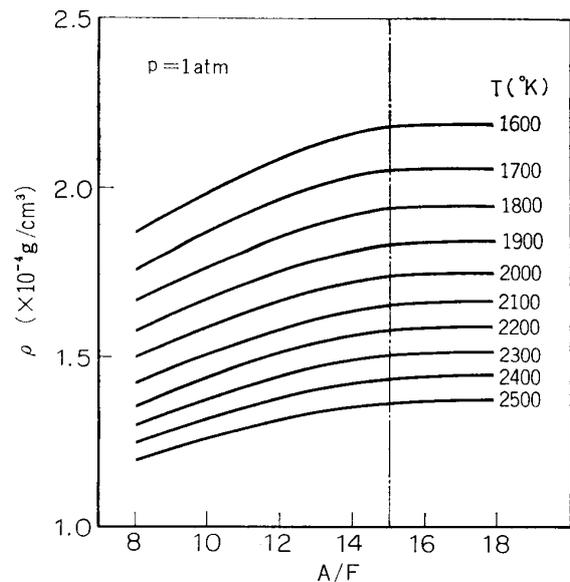


FIG. 15. Density of burned gas mixtures.

coefficient  $\mu$  and thermal conductivity  $\lambda$  of burned gas mixtures are calculated for the air-fuel ratio from 8 to 18, the temperature range from 1600 to 2500°K and the pressure range from 1 to 30 atm.

The burned gas mixtures of *n*-octane by air are considered, being in equilibrium at each temperature as mentioned in introduction. The dependence of viscosity coefficient  $\mu$  and thermal conductivity  $\lambda$  on the temperature is large as shown in Figs. 12 and 13, but the dependence of viscosity coefficient  $\mu$  on the pressure is small as seen in Fig. 14. Thermal conductivity  $\lambda$  is a function of the temperature and concentrations, but not the pressure as shown in Eqs. (14). The small influ-

TABLE 6. Viscosity Coefficient of Burned Gas Mixtures. (p=1 atm)  
 $\mu (\times 10^{-4} \text{ g/cm}\cdot\text{sec})$

T°K \ A/F	8	10	12	14	15	16	18
1600	5.0	5.1	5.1	5.2	5.2	5.2	5.2
1700	5.2	5.3	5.3	5.4	5.4	5.4	5.4
1800	5.4	5.5	5.6	5.6	5.6	5.6	5.6
1900	5.6	5.7	5.8	5.8	5.8	5.9	5.9
2000	5.8	5.9	6.0	6.0	6.1	6.1	6.1
2100	6.0	6.1	6.2	6.3	6.3	6.3	6.3
2200	6.2	6.3	6.4	6.5	6.5	6.5	6.5
2300	6.4	6.5	6.6	6.7	6.7	6.7	6.7
2400	6.6	6.7	6.8	6.8	6.9	6.9	6.9
2500	6.8	6.9	7.0	7.0	7.0	7.0	7.0

TABLE 7. Thermal Conductivity of Burned Gas Mixtures. (p=1 atm)  
 $\lambda (\times 10^{-4} \text{ cal/cm}\cdot\text{sec}\cdot\text{°K})$

T°K \ A/F	8	10	12	14	15	16	18
1600	4.8	3.7	3.0	2.5	2.4	2.3	2.3
1700	5.0	3.9	3.2	2.7	2.5	2.5	2.4
1800	5.2	4.1	3.3	2.9	2.7	2.7	2.6
1900	5.5	4.2	3.5	3.0	2.9	2.8	2.7
2000	5.7	4.4	3.6	3.2	3.0	3.0	2.9
2100	5.9	4.6	3.8	3.3	3.2	3.1	3.1
2200	6.2	4.8	4.0	3.5	3.4	3.3	3.2
2300	6.4	5.0	4.2	3.7	3.6	3.5	3.4
2400	6.6	5.2	4.4	3.9	3.8	3.7	3.5
2500	6.8	5.4	4.6	4.1	3.9	3.8	3.7

TABLE 8. Density of Burned Gas Mixtures.  
 $\rho (\times 10^{-4} \text{ g/cm}^3) \text{ (p=1 atm)}$

T°K \ A/F	8	10	12	14	15	16	18
1600	1.86	1.98	2.07	2.15	2.18	2.18	2.18
1700	1.75	1.87	1.95	2.02	2.05	2.05	2.05
1800	1.66	1.76	1.84	1.91	1.94	1.94	1.94
1900	1.57	1.67	1.75	1.81	1.83	1.83	1.84
2000	1.49	1.59	1.66	1.72	1.74	1.74	1.74
2100	1.42	1.51	1.58	1.63	1.65	1.66	1.66
2200	1.35	1.44	1.51	1.56	1.57	1.58	1.58
2300	1.29	1.38	1.44	1.49	1.50	1.50	1.51
2400	1.24	1.32	1.38	1.42	1.43	1.43	1.43
2500	1.19	1.26	1.32	1.35	1.36	1.36	1.37

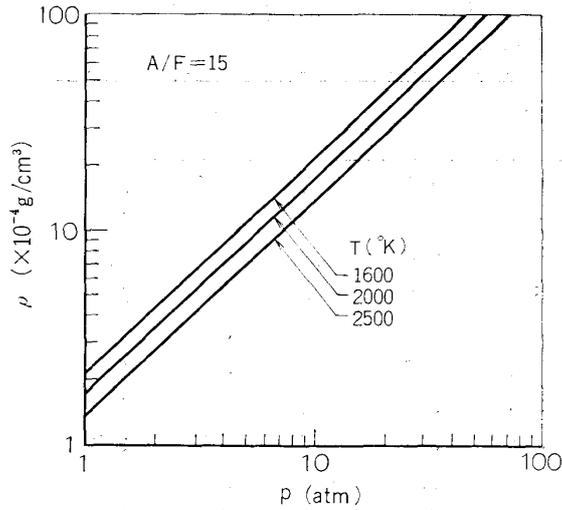


FIG. 16. Density of burned gas mixtures.

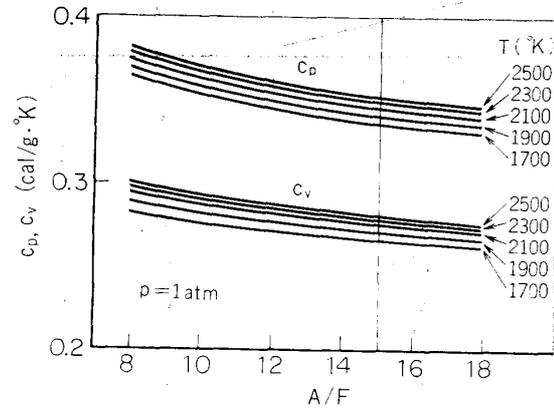


FIG. 17. Heat capacity at constant pressure and constant volume of burned gas mixtures.

TABLE 9. Heat Capacity at Constant Pressure of Burned Gas Mixtures ( $p=1$  atm)

		$C_p$ (cal/g·°K)						
$T^{\circ}\text{K}$	A/F	8	10	12	14	15	16	18
		1600	0.360	0.348	0.341	0.335	0.333	0.331
1700	0.364	0.352	0.344	0.339	0.336	0.334	0.330	
1800	0.367	0.354	0.347	0.341	0.339	0.337	0.333	
1900	0.369	0.357	0.349	0.344	0.342	0.339	0.335	
2000	0.372	0.359	0.352	0.346	0.344	0.342	0.337	
2100	0.374	0.362	0.354	0.348	0.346	0.344	0.339	
2200	0.376	0.364	0.356	0.350	0.348	0.345	0.341	
2300	0.378	0.365	0.357	0.352	0.349	0.347	0.343	
2400	0.379	0.367	0.359	0.353	0.350	0.348	0.344	
2500	0.381	0.368	0.360	0.354	0.351	0.349	0.345	

ences of the pressure on the thermal conductivity  $\lambda$  comes from changes in the equilibrium concentrations depending on the pressure. Therefore, the values of viscosity coefficient  $\mu$  and thermal conductivity  $\lambda$  at  $p=1$  atm are listed in Tables 6 and 7. The values of density of burned gas mixtures  $\rho$  are shown in Figs. 15 and 16 and in Table 8. The influence of the pressure on the values of density of burned gas mixtures is attributed to the pressure change, but scarcely to the concentration change depending on the pressure as shown in Fig. 16. The values of heat capacity at constant pressure  $C_p$  and at constant volume  $C_v$  are shown in Fig. 17 and in Tables 9 and 10. These values are calculated by NASA Tables [8]. The dependence of these values on the pressure is also very small.

TABLE 10. Heat Capacity at Constant Volume of Burned Gas Mixtures. ( $p=1$  atm)  
 $C_v$  (cal/g·°K)

T°K \ A/F	8	10	12	14	15	16	18
1600	0.279	0.272	0.268	0.265	0.264	0.262	0.258
1700	0.282	0.275	0.271	0.268	0.267	0.265	0.261
1800	0.285	0.278	0.274	0.271	0.270	0.268	0.263
1900	0.288	0.281	0.276	0.273	0.272	0.270	0.266
2000	0.290	0.283	0.279	0.276	0.274	0.272	0.268
2100	0.293	0.285	0.281	0.278	0.276	0.274	0.270
2200	0.295	0.287	0.283	0.279	0.278	0.276	0.271
2300	0.296	0.289	0.284	0.281	0.279	0.277	0.273
2400	0.298	0.290	0.285	0.282	0.279	0.277	0.274
2500	0.299	0.292	0.286	0.282	0.280	0.278	0.274

## 8. CONCLUSION

The transport properties of the burned gas mixtures were found to be estimated sufficiently enough by the approximate equations to the kinetic theory equations for the multicomponent gas mixtures. The transport properties of each species in burned gas mixtures are calculated on the basis of the rigid-sphere potential. The collision diameters  $\sigma_i$  of the molecular species CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, NO and O<sub>2</sub> in the burned gas mixtures are calculated from the experimental data of their viscosity coefficients for temperature range from 300 to 1273°K on the basis of the rigid-sphere potential and expressed as a function of temperature. With these collision diameters, we can calculate the viscosity coefficient  $\mu_i$ , thermal conductivity  $\lambda_i$ , and binary diffusion coefficient  $\mathcal{D}_{ij}$  of each species for temperature range extrapolated from 300 to 2500°K based on the rigid-sphere potential and we found that good agreement exists between the experimental data of transport properties and the calculated results. As we could not find their experimental data of viscosity coefficient in references for atomic H, N and O and radical species OH, the accurate estimate for the calculated values of their viscosity coefficients and thermal conductivities could not be obtained. However, for the present work, their calculated values are found to be sufficiently enough approximate values.

In calculation of the multicomponent diffusion coefficient  $D_{ij}$ , it is not necessary to consider the change in mole fraction, but only the change in temperature must be taken into account. The thermal diffusion coefficient is of no significance compared with the ordinary diffusion.

*Department of Jet Propulsion  
Institute of Space and Aeronautical Science  
University of Tokyo, Tokyo  
December 10, 1973*

## REFERENCES

- [1] Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., *Molecular Theory of Gases and Liquids*, John Wiley & Sons, New York, (1964).
- [2] Golubev, I. F., *Viscosity of Gases and Gas Mixtures*, Israel Program for Scientific Translations, Jerusalem, (1970).
- [3] Hirschfelder, J. O., *J. Chem. Phys.*, **26**, 282, (1957).
- [4] Bird, R. B., Stewart, W. E. and Lightfoot, E. N., *Transport Phenomena*, John Wiley & Sons, New York, (1960).
- [5] Muckenfuss, C. & Curtiss, C. F., *J. Chem. Phys.*, **29**, 1273, (1958).
- [6] Mason, E. A. & Saxena, S. C., *J. Chem. Phys.*, **31**, 511, (1959).
- [7] Touloukian, Y. S., Liley, P. E. and Saxena, S. C., *Thermophysical Properties of Matter, The TPRC Data Series, 3*, Plenum, New York, (1970).
- [8] NASA-SP 3001, (1963).