The Thermal Conductivity and Diffusivity of Gases for Temperatures to 10,000°K.

G. P. MATHUR and GEORGE THODOS

Northwestern University, Evanston, Illinois

A generalized method has been developed for the prediction of the diffusivity and thermal conductivity of nonpolar gases for temperatures up to 10,000°K. This method is applicable to monatomic gases and to diatomic gases existing in their molecular and dissociated states. Dimensional analysis has been used to obtain relationships for self- and mutual diffusivities and for the translational contribution to the thermal conductivity of these substances. For the internal contribution to thermal conductivity, a modified Eucken-factor relationship is presented. Furthermore, relationships have been developed for the calculation of these transport properties for the equilibrium mixture of a dissociating gas.

Current advances in space technology have created a need for making available the transport properties of gases at extreme conditions of temperature and pressure. While adequate experimental work has been reported at high pressures for gases of simple molecular structure, similar work at temperatures above 1,600°K. presents problems for the selection of suitable materials of construction (*6*). Because of these limitations, it becomes necessary to devise methods for predicting the behavior of gases at high temperatures where no experimental values are available.

Amdur and co-workers (*1, 2, 3, 5*) utilize molecular beam measurements in order to establish intermolecular potentials for temperatures above 5,000°K. For the intermediate temperature range, 1,000° to 5,000°K., they have made use of blends or combinations of functions valid at low temperatures with those derived from the beam experiments. The potentials thus obtained have been utilized by Mason and co-workers (*4, 13, 14*) to determine the collision integrals at these high temperatures for each substance studied. Once these collision integrals become available, the corresponding transport properties can be calculated in a relatively simple manner. Although the molecular beam approach is very valuable, its application is restricted to a particular substance, and therefore it lacks generality. A generalized approach for the prediction of transport properties from known physical properties should prove useful. In this connection, Mathur and Thodos (*11*) have presented a generalized method for the prediction of viscosities of gases for temperatures up to 10,000°K. Following the same basic concepts, the present study is concerned with the development of a generalized method for the prediction of thermal conductivities and diffusivities of nonpolar gases at elevated temperatures.

SELF-DIFFUSIVITY AND MUTUAL DIFFUSIVITY

The first approximation to the diffusion coefficient in terms of the collision integral is given by the expression

$$\mathcal{D}_{ij} = \frac{262.8 \times 10^{-5}\, T^{3/2}}{\pi \sigma_{ij}{}^2 \Omega^{(1,1)}[T_N]} \sqrt{\frac{M_i + M_j}{2M_iM_j}} \qquad (1)$$

If species i and j are the same, then $\mathcal{D}_{ii}$ represents the self-diffusion coefficient. For the calculation of $\mathcal{D}_{11}$, values for the collision integral $\Omega^{(1,1)}[T_N]$ are available in the literature (9) for the low-temperature range. For elevated temperatures, Mason et al. (*4, 13, 14*) have presented collision integrals and self-diffusivities for specific gases. A generalized method for predicting this transport property can be developed through a dimensional analysis approach. Thus, if the product $\pi\mathcal{D}_{11}$ is considered to be a function of the following properties

$$\pi\mathcal{D}_{11} = f(T_c, P_c, v_c, R, M, T) \qquad (2)$$

the following relationship results:

$$(\pi\mathcal{D}_{11})\ \delta = \alpha z_c{}^m T_R{}^n \qquad (3)$$

where the modulus $\delta = M^{1/2}/P_c{}^{2/3}T_c{}^{5/6}$. The diffusivity values reported by Mason et al. (*4, 13, 14*) from 1,000° to 10,000°K. were used to produce the relationship shown in Figure 1. In this figure the product $(\pi\mathcal{D}_{11})\delta$ is plotted against T_R for all the monatomic gases and the undissociated and completely dissociated forms of the diatomic

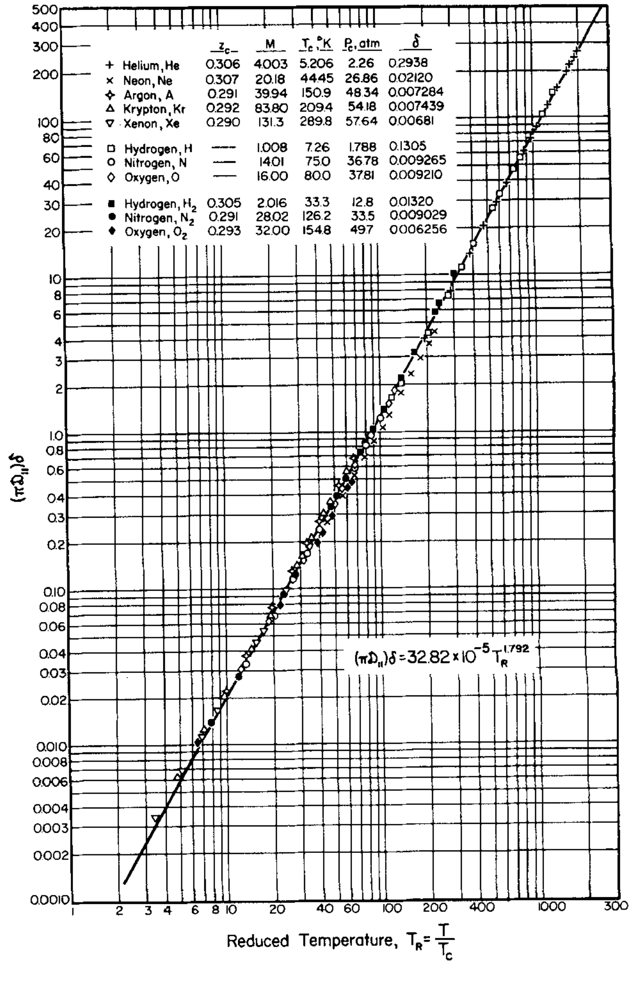


Fig. 1. Generalized relationship between the self-diffusivity modulus $(\pi\mathcal{D}_{11})\ \delta$ and reduced temperature T_R.

gases, hydrogen, nitrogen, and oxygen. For the dissociated form of the diatomic gases, the critical constants used were those developed previously for the correlation of viscosities at high temperatures (*11*). In that work, the hypothetical critical constants for the dissociated species were developed from the existing information on the force laws and from the correspondence of these species to the monatomic gases. Recently, an interesting review of the current literature on the force law between two hydrogen atoms has been presented by Coulson and Haigh (*8*). As a result of their analysis, Coulson and Haigh have placed the potential energy minimum at a nuclear separation of 2.5Å. It is interesting to compare this value with the value of $\sigma = 2.572$Å used by Mathur and Thodos (*11*) in their high-temperature viscosity studies. The values of all these substances produce a relationship that is unique and is also linear on log-log coordinates. The fact that all these substances, which do not have the same critical compressibility factor z_c, produce a single relationship indicates that $m \approx 0$ and therefore the relationship of Figure 1 can be represented analytically as follows:

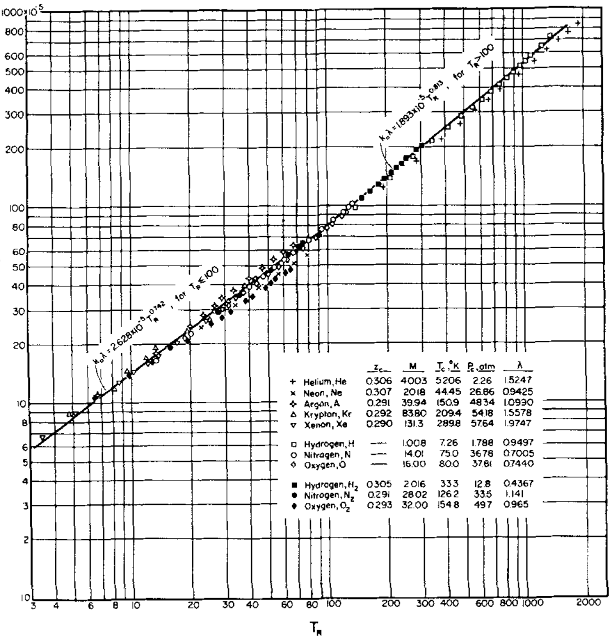
$$(\pi \mathfrak{D}_{11})\delta = 32.82 \times 10^{-5} T_R^{1.792} \qquad (4)$$

For a dissociating gas, the mutual diffusion coefficient $\mathfrak{D}_{ij}$ becomes significant. For a binary mixture, this coefficient is independent of composition in the first degree of approximation. In this study, a method has been devised for the prediction of this coefficient from a knowledge of the critical properties of the pure species of the mixture.

With the exception of hydrogen, the mutual diffusivity coefficients for a dissociating mixture can be rather easily predicted with Equation (4) by using geometrical averages of the critical constants and molecular weights. When compared with the values reported by Mason et al. (*14*), the deviations for nitrogen mixtures and oxygen mixtures were found to be 0.94 and 2.1%, respectively. The reason for the abnormal behavior of hydrogen mixtures may be due to the rather unusual collision integrals for this system (*13*). Consequently, the properties for hydrogen mixtures are not intermediate to those of the corresponding pure species. This effect has been observed for the viscosity (*11*) and is also apparent in this study for the thermal conductivity of hydrogen mixtures. Inasmuch as this represents an unusual and rare behavior and is not likely to be encountered for substances heavier than hydrogen, the following equation is recommended for the mutual diffusivity of hydrogen mixtures:

$$\pi \mathfrak{D}_{12} = 5.475 \times 10^{-3} T_R^{1.922} \qquad (5)$$

where $T_c = 15.54$°K. In Equation (5), the subscripts 1 and 2 refer to monatomic and diatomic species, respectively.



	z_c	M	T_c, °K	P_c, atm	λ
+ Helium, He	0.306	4.003	5.206	2.26	1.5247
× Neon, Ne	0.307	20.18	44.45	26.86	0.9425
✧ Argon, A	0.291	39.94	150.9	48.34	1.0930
△ Krypton, Kr	0.292	83.80	209.4	54.18	1.5578
▽ Xenon, Xe	0.290	131.3	289.8	57.64	1.9747
□ Hydrogen, H	—	1.008	7.26	1.788	0.9497
○ Nitrogen, N	—	14.01	75.0	36.78	0.7005
◇ Oxygen, O	—	16.00	80.0	37.81	0.7440
■ Hydrogen, H_2	0.305	2.016	33.3	12.8	0.4367
● Nitrogen, N_2	0.291	28.02	126.2	33.5	1.141
◆ Oxygen, O_2	0.293	32.00	154.8	49.7	0.965

Fig. 2. Generalized relationship for the translational contribution to thermal conductivity.

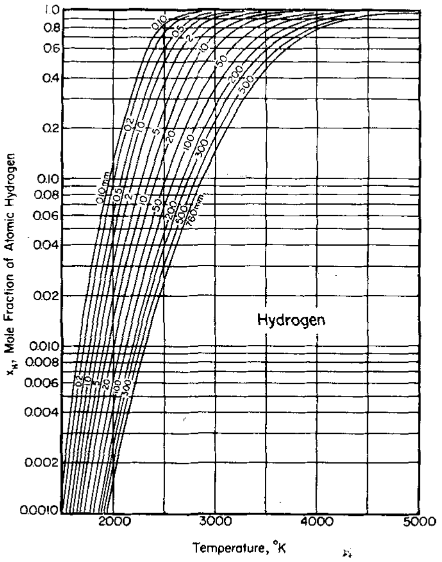


Fig. 3. Isobaric relationships between x_H and temperature for hydrogen at high temperatures.

THERMAL CONDUCTIVITIES

Generalized Relationships for Undissociated and Completely Dissociated Gases

The thermal conductivity of undissociated and completely dissociated gases, known as the *frozen thermal conductivity*, k_f, represents the sum of a translational contribution k_o and an internal contribution k_i:

$$k_f = k_o + k_i \qquad (6)$$

In terms of collision integrals, the translational contribution to thermal conductivity of a pure substance is given by

$$k_o = 19.891 \times 10^{-5} \frac{\sqrt{T/M}}{\sigma^2 \, \Omega^{(2,2)} \, [T_N]} \qquad (7)$$

When one follows a dimensional analysis approach, the translational thermal conductivity can be considered as being dependent on the following fundamental properties of the substance under consideration:

$$k_o = f(T_c, P_c, v_c, R, M, T) \qquad (8)$$

The following expression results from this analysis:

$$k_o\lambda = \beta z_c^{\,p} T_R^{\,s} \qquad (9)$$

where $\lambda = T_c^{1/6} M^{1/2} / P_c^{2/3}$. The k_o values reported by Mason et al. (*4, 13, 14*) from 1,000° to 10,000°K. for the monatomic gases and hydrogen, nitrogen, and oxygen in their diatomic and completely dissociated states were utilized to obtain $k_o\lambda$ which, when plotted against reduced temperature, produced the relationship of Figure 2. The uniqueness of this relationship indicates that exponent p of Equation (9) is essentially zero, and therefore

$$k_o\lambda = 2.628 \times 10^{-5} T_R^{0.742} \text{ for } T_R \leq 100 \qquad (10)$$

and

$$k_o\lambda = 1.893 \times 10^{-5} T_R^{0.813} \text{ for } T_R > 100 \qquad (11)$$

For gases with internal degrees of freedom like diatomic nitrogen, oxygen, and hydrogen, the internal contribution to the thermal conductivity must be accounted for. When one follows a modified Eucken type of approach (*7*), it is possible to show that

$$k_o = \frac{5}{2}\mu C_v' \tag{12}$$

and

$$k_f = \left[\frac{15}{4}(\gamma - 1) + \frac{1}{2}u_{11}(5 - 3\gamma)\right] C_v \mu \tag{13}$$

where $C_v' = \dfrac{3(\gamma - 1)}{2} C_v$ and u_{11} is a numerical factor that depends on the nature of the molecular model employed. Since the force laws for the molecules are not constant over a range of temperature, u_{11} will in general vary over the temperature range under consideration. However, it is reasonably accurate to consider a Maxwellian model for which $u_{11} = 1.55$. For such a model, Equations (12) and (13) can be solved to yield the following relationship:

$$\frac{k_i}{k_o} = \frac{3.875 - 2.325\gamma}{3.75(\gamma - 1)} \tag{14}$$

The values of γ are obtained from available tabulated heat capacities (*9*). If the electronic excitation is neglected, it is seen that the heat capacity attains the maximum value of $\frac{9}{2}R$ above 3,000°, 3,500°, and 1,500°K. for hydrogen, nitrogen, and oxygen, respectively. Consequently, above these three temperatures, Equation (14) simplifies to $k_i/k_o = 0.8269$.

Thermal Conductivity of Partially Dissociated Gases

The first essential step towards the calculation of the thermal conductivity of a dissociating gas is the establishment of its equilibrium composition. For a diatomic gas, the dissociation reaction is

$$\frac{1}{2}A_2 \rightleftarrows A \tag{15}$$

For this reaction, the equilibrium mole fraction of the atomic species can be computed from the expression

$$x_A = \frac{2}{1 + \sqrt{\dfrac{4\pi}{K^2} + 1}} \tag{16}$$

where $K = p_A/\sqrt{p_{A_2}}$ is the equilibrium constant for the reaction. Values of K for some diatomic gases can be found elsewhere (*12*). Typical isobaric relationships between the equilibrium composition and temperature are presented in Figure 3 for hydrogen.

The frozen thermal conductivity of a dissociated gas can be calculated by the use of the following simple relationship:

$$k_{f,\mathrm{mixt}} = k_{o,\mathrm{mixt}} + k_{A_2,\mathrm{int}} x_{A_2} \tag{17}$$

where $k_{A_2,\mathrm{int}}$ is obtained from Equation (14), while $k_{o,\mathrm{mixt}}$ is obtained by using combination rules for the parameters λ and T_c and Figure 2. For a substance like hydrogen which exhibits excessive quantum deviations, these parameters can be calculated as follows:

$$\lambda' = \frac{[T_{cA}x_A + T_{cA_2}x_{A_2}]^{1/6}\,[M_A x_A + M_{A_2}x_{A_2}]^{1/2}}{[P_{cA}x_A + P_{cA_2}x_{A_2}]^{2/3}} \tag{18}$$

and

$$T_c' = T_{cA}x_A + T_{cA_2}x_{A_2} \tag{19}$$

For normal behaving substances, these combination rules become

$$\lambda' = \lambda_A x_A + \lambda_{A_2} x_{A_2} \tag{20}$$

and

$$T_c' = T_{cA}x_A + T_{cA_2}x_{A_2} \tag{21}$$

Values for $k_{f,\mathrm{mixt}}$ calculated for nitrogen, oxygen, and hydrogen, when compared with corresponding values reported by Mason et al. (*13, 14*), show good agreement with nitrogen and oxygen, for which deviations of 0.86 and −2.58% result. As already pointed out, the behavior of hydrogen mixtures, as reported by Mason, is rather peculiar. Consequently, a comparison between values calculated with Equations (17), (18), and (19) and those reported by Mason et al. (*13, 14*) show a relatively large deviation of 12.2%.

An additional contribution to the thermal conductivity follows from the dissociation reaction. This contribution must be added to the frozen thermal conductivity in order to obtain the effective thermal conductivity for the mixture as follows:

$$k_{\mathrm{eff}} = k_{f,\mathrm{mixt}} + k_r \tag{22}$$

In Equation (22) the contribution due to the heat of dissociation is

$$k_r = \frac{\pi \mathcal{D}_{12}}{RT}\,\frac{(\Delta H)^2}{RT^2}\,\frac{x_A x_{A_2}}{(1 + x_A)^2} \tag{23}$$

Values of the heat of dissociation ΔH are available in the literature (*9*) and approach a constant value as the heat capacity attains its maximum value.

CONCLUSION

A generalized method for the calculation of self-diffusivities, mutual diffusivities, and thermal conductivities of gases up to temperatures of 10,000°K. has been developed. This method can be used to predict, in a relatively simple manner, these transport properties for monatomic, diatomic, and partially dissociated gases. The validity of this method was tested, and it was found to be in good agreement with transport property values derived from molecular beam measurements.

NOTATION

C_p = heat capacity at constant pressure, cal./g.-mole °K.
C_v = heat capacity at constant volume, cal./g.-mole °K.
C_v' = translational contribution to heat capacity at constant volume, $[3(\gamma - 1)/2]C_v$, cal./g.-mole °K.
k_{eff} = effective thermal conductivity of a dissociating gas, cal./sec. cm. °K.
k_f = frozen thermal conductivity, $k_o + k_i$, cal./sec. cm. °K.
k_i = internal contribution to the thermal conductivity, cal./sec. cm. °K.
k_o = translational contribution to the thermal conductivity, cal./sec. cm. °K.
K = equilibrium constant for dissociation reaction, $p_A/\sqrt{p_{A_2}}$, atm.$^{1/2}$
H = molar enthalpy, cal./g.-mole
M = molecular or atomic weight
m, n = exponents, Equation (3)
p, s = exponents, Equation (9)
p_i = partial pressure of species i
P_c = critical pressure, atm.
R = gas constant
T = temperature, °K.
T_c = critical temperature, °K.
T_c' = pseudocritical temperature, °K.

T_N = normalized temperature, $T/\frac{\epsilon}{\kappa}$
T_R = reduced temperature, T/T_c
u_{11} = numerical factor, Equation (13)
v_c = critical volume, cc./g.-mole
x_i = mole fraction of species i
z_c = critical compressibility factor, $P_c v_c / R T_c$

Greek Letters

α = constant, Equation (3)
β = constant, Equation (9)
γ = ratio of heat capacities, C_p/C_v
δ = diffusivity modulus, $M^{1/2}/P_c^{2/3}T_c^{5/6}$
$\mathcal{D}_{ij}$ = coefficient of diffusion for species i and j
ϵ = maximum energy of interaction between two particles, erg.
κ = Boltzmann constant, 1.3805×10^{-16} erg./°K.
λ = thermal conductivity modulus, $T_c^{1/6}M^{1/2}/P_c^{2/3}$
λ' = pseudothermal conductivity modulus
μ = viscosity, g./sec. cm.
π = pressure, atm.
σ = collision diameter, Å.
$\Omega^{(1,1)}[T_N]$ = collision integral for diffusivity
$\Omega^{(2,2)}[T_N]$ = collision integral for thermal conductivity

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Particle Flow Patterns in a Fluidized Bed

R. M. MARSHECK and ALBERT GOMEZPLATA
University of Maryland, College Park, Maryland

A modified thermistor anemometer probe was used to measure solid particle flow patterns in a 9.5-in. diameter fluidized bed. The probe was calibrated and found to measure the direction and mass velocity of the silica-alumina cracking catalyst used. Flow patterns were determined at heights of 6.5, 12.5, 18.5, and 24.5 in. above the support plate with superficial air velocity from 0.25 to 1.00 ft./sec. and bed depths of 14 to 30 in.

Radial flow patterns were found not to be symmetrical about the axis of the bed but were similar at angles of 60 deg. This indicated that there were six similar particle flow pattern sections around the column axis.

The percentage of the cross-sectional area of the fluidized bed through which the particle flow is upward was found to be approximately 60%. There was no definite dependence of this area on any of the variables studied.

The catalyst bulk circulation rate, defined as the average mass velocity of the particles at a given cross section in a fluidized bed without regard to the direction of flow, was determined for each fluidization condition and correlated as a function of the superficial air velocity and the ratio of the distance above the support plate to the height of the fluidized bed.

It has generally been proposed that solids travel down a fluidized bed close to the wall and up through the center of the bed with cross flow between the center and the wall taking place at several elevations in the bed. These speculations about the circulation pattern are based almost entirely on visual observation at the surface of the bed, and the travel of particles within the bed remains in doubt.

Particle velocities along the column wall were studied by Toomey and Johnstone (*16*) and Massimilla and Westwater (9) using high-speed photographic techniques. Particle velocities up to 6 ft./sec. were noted, with very abrupt changes in direction taking place. Side motion of the particles was relatively mild.

Leva and Grummer (*5*) distributed dyed particles on the top of a fluidized bed and measured the time required for the uniform distribution of the dyed particles to take place in the bed, as determined by visual observation.

Others (*2, 4, 6, 10, 12, 13, 14*) have used tagged particles to study the rate of mixing of solids.

No direct measurements of particle flow patterns in the interior of a fluidized bed have been found in the literature, and this investigation probably represents the first reported investigation of these flow patterns.

GENERAL METHOD

Hot-wire anemometers have been widely used to measure point velocities in a moving stream of fluid (*11*). In

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R. M. Marsheck is at present with Phillips Petroleum Company, Bartlesville, Oklahoma.