The Viscosity of Nonpolar Gas Mixtures at Moderate and High Pressures

DAVID E. DEAN and LEONARD I. STIEL

Syracuse University, Syracuse, New York

A method has been developed for the calculation of the viscosity of nonpolar gas mixtures at moderate and elevated pressures from the molecular weights and critical constants of the components. By the use of available experimental data and appropriate pseudocritical constant rules, results obtained previously for the viscosity of pure gases have been extended to mixtures. Viscosity values calculated by the method developed in this study for a number of nonpolar gas mixtures were found to reproduce reported values with a high degree of accuracy.

Reliable methods have recently been developed for the prediction of the viscosity of pure substances in the dilute and dense gaseous regions. Similar generalized relationships are not available at present for the calculation of the viscosity of gas mixtures at elevated pressures. Accurate values of this property for gaseous mixtures are required in many important applications. It is apparent that reliance on experimental data for the viscosity values of gaseous mixtures is hopelessly inadequate, because of the wide ranges of composition, temperature, and pressure encountered.

Rigorous theoretical expressions are available only for the transport properties of gaseous mixtures at approximately atmospheric pressure. Lee, Starling, Dolan, and Ellington (*51*) have recently presented a semiempirical relationship for the calculation of the viscosity of binary mixtures of methane, ethane, propane, and *n*-butane. The only generalized methods that have been suggested for the calculation of the viscosity of dense gaseous mixtures are modifications of correlations for pure components in which the group μ/μ^* (or μ/μ_c) is empirically related to T_R and P_R through the available experimental data (*18*, *87*). The critical temperatures and pressures of the mixtures are calculated from the critical constants of the pure components by the use of the linear combination rules proposed by Kay (*43*). However, it is well established that reduced state correlations of this type are specific only to individual substances or substances having a similar nature, and that a generalized correlation must contain an additional parameter (such as the critical compressibility factor of the substance) to account for the size and shape of the molecules (*7*).

For pure substances, Jossi, Stiel, and Thodos (*42*) have developed analytical relationships between the residual viscosity group, $(\mu - \mu^*)\xi$, and the reduced density of the substance from experimental data for twelve substances (including monatomic and diatomic gases, hydrocarbons, and carbon dioxide). This method for the prediction of the viscosity of pure substances does not possess the limitations of the previous correlations for the reduced viscosity which contain an insufficient number of parameters to be applicable to a wide range of substances. In addition, analytical expressions are much more suitable for computer calculations than graphical correlations, which require the storage of a large number of values and tedious interpolation calculations. Therefore, in the present study an approach similar to that employed by Jossi, Stiel, and Thodos (*42*) has been used to develop relationships for the calculation of viscosity values of gaseous mixtures over wide ranges of temperatures and pressures from the appropriate critical constants of the mixtures.

THE VISCOSITY OF GASEOUS MIXTURES AT MODERATE PRESSURES

The rigorous kinetic theory expression for the viscosity of an *n* component mixture at atmospheric pressure and temperatures below approximately 1,000°K. (*34*) can be expressed as follows by the elimination of second-order effects (*13*):

$$\mu^* = \sum_{i=1}^{n} \frac{\mu_i^*}{1 + \sum\limits_{\substack{k=1 \\ k\neq i}}^{n} \psi_{ik} \dfrac{x_k}{x_1}} \tag{1}$$

where $\psi_{ik} = 6/5\, A^*_{ik} \dfrac{RT}{PM_i} \dfrac{\mu_i^*}{D^*_{ik}}$ and $A^*_{ik} = \dfrac{\Omega_{ik}^{(2,2)*}}{\Omega_{ik}^{(1,1)*}}$, the ratio of the reduced collision integrals for viscosity and diffusivity. Through semitheoretical considerations based on the rigid sphere model proposed by Sutherland (*74*), Wilke (*15*, *91*) has developed the following relationship for the ψ_{ik} values in Equation (1):

$$\psi_{ik} = \frac{[1 + (\mu_i^*/\mu_k^*)^{1/2}(M_k/M_i)^{1/4}]^2}{(4\sqrt{2})\,[1 + (M_i/M_k)]^{1/2}} \tag{2}$$

Equation (2) can be derived from Equation (1) with the approximations that $A^*_{ik} = A^*_i$ and $[\Omega_{ik}^{(1,1)*}/\Omega_i^{(1,1)*}]^{1/2} = 1.0$ (*19*). Since the reduced collision integrals $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ are both slowly varying functions of temperature for a realistic intermolecular model, such as the Lennard-Jones potential, these approximations are excellent and the Wilke equation is therefore essentially equivalent to the rigorous kinetic theory expression. Brokaw (*14*) has presented alignment charts that simplify the calculation of viscosities from Equations (1) and (2).

Several investigators (*17*, *32*) have recommended the use of the following equation for the calculation of viscosity values for multicomponent hydrocarbon mixtures at moderate pressures:

$$\mu^* = \frac{\sum\limits_i \mu_i x_i \sqrt{M_i}}{\sum x_i \sqrt{M_i}} \tag{3}$$

For binary mixtures, Equation (3) can be written as

$$\mu^* = \frac{\mu_1}{1 + \dfrac{x_2}{x_1}\sqrt{\dfrac{M_2}{M_1}}} + \frac{\mu_2}{1 + \dfrac{x_1}{x_2}\sqrt{\dfrac{M_1}{M_2}}} \tag{4}$$

A comparison between Equations (1) and (4) indicates that Equation (4) should be more accurate for mixtures whose components have molecular weights and force constants that are nearly equal (*19*). Equation (4) also implies that $\psi_{12} = \sqrt{M_2}/\sqrt{M_1}$ and $\psi_{21} = \sqrt{M_1}/\sqrt{M_2}$. Wright and Gray (*93*) have shown that for binary mixtures there is a considerable range of pairs of ψ_{12} and ψ_{21} values with which viscosities can be calculated with good accuracy. The use of Equation (4) is restricted to binary systems that do not exhibit a maximum with respect to variations in their composition. However, this limitation is not serious, since only certain binary mixtures that contain either hydrogen, helium, or one polar constituent can exhibit such a maximum (*35*).

Although viscosity values for nonpolar gas mixtures at moderate pressures can be calculated to within the experimental accuracy from Equations (1) and (2) or Equation (3), these relationships have the disadvantage that viscosities must be initially computed for each of the pure components. Therefore, in the present study, relationships between $\mu^*\xi$ and reduced temperature similar to those presented by Stiel and Thodos (*71*) for pure nonpolar substances have been developed for gaseous mixtures, which permit the direct calculation of viscosity values from appropriate critical constants for the mixture. Equations of this type are also more convenient for use in conjunction with a relationship between $(\mu - \mu^*)\xi$ and ρ_R for the calculation of viscosities of mixtures at elevated pressures. And since reliable viscosity data are available for binary and multicomponent mixtures at atmospheric pressure, the establishment of a unique relationship between $\mu^*\xi$ and T_R for gaseous mixtures provides a convenient and accurate test of the various methods available for the calculation of the pseudocritical constants of mixtures.

PSEUDOCRITICAL CONSTANTS OF GASEOUS MIXTURES

For gaseous mixtures, the use of experimental values of critical constants for the calculation of volumetric properties from correlations based on the principle of corresponding states has been found to lead to large errors (*43*). A hypothetical pure substance has to be defined whose isochors are identical to the isochors of the mixture. The critical constants of the hypothetical substance are then the pseudocritical constants of the mixture. Since these pseudocritical constants cannot be established experimentally, several methods have been proposed for their estimation from the critical constants of the pure components (*40, 43, 52, 59*). The most widely used relationships for the calculation of pseudocritical constants are the linear rules proposed by Kay (*43*)

$$T_{cm} = \sum_i x_i T_{c_i} \tag{5}$$

$$P_{cm} = \sum_i x_i P_{c_i} \tag{6}$$

Joffee (*40*) has developed the following relationships by applying the van der Waals equation of state to binary mixtures

$$\frac{T_{cm}}{P_{cm}^{1/2}} = A = \frac{x_1 T_{c_1}}{P_{c_1}^{1/2}} + \frac{x_2 T_{c_2}}{P_{c_2}^{1/2}} \tag{7}$$

$$\frac{T_{cm}}{P_{cm}} = B = \frac{x_1^2 T_{c_1}}{P_{c_1}} + \frac{x_2 T_{c_2}}{P_{c_2}} + \frac{1}{4} x_1 x_2 \left[(T_{c_1}/P_{c_1})^{1/3} + (T_{c_2}/P_{c_2})^{1/3} \right]^3 \tag{8}$$

and $T_{cm} = A^2/B$, $P_{cm} = T_{cm}/B$. Equations (8) and (9) have been found to be slightly more accurate for use in PVT correlations than Equations (6) and (7). In a very complete study of the volumetric behavior of binary gas mixtures, Prausnitz and Gunn (*59*) found that Equation (5) is approximately correct for critical temperatures, but that the use of the linear rule for critical pressures expressed in Equation (6) could lead to large errors in many cases. However, for a ratio of the critical volumes of the pure components of less than 3.0, Prausnitz and Gunn found the following equations to be satisfactory for the calculation of the pseudocritical volume and pseudocritical compressibility factor of an n component mixture:

$$V_{cm} = \sum_i x_i V_{c_i} \tag{9}$$

$$z_{cm} = \sum_i x_i z_{c_i} \tag{10}$$

TABLE 1. AVERAGE DEVIATIONS BETWEEN CALCULATED AND EXPERIMENTAL VISCOSITIES FOR GASEOUS MIXTURES AT MODERATE PRESSURES

			Pseudocritical methods			Other methods	
System	Reference	Number of points	Prausnitz and Gunn	Kay	Joffe	Wilke	Equation (4)
N_2-O_2	*49, 84*	28	0.96%	1.05%	0.87%	0.94%	0.81%
O_2-CO	*84*	18	1.30	0.70	1.04	0.35	0.43
N_2-CO	*84*	24	0.77	0.75	0.70	0.62	0.62
N_2-NO	*84*	6	2.00	4.74	2.88	1.89	1.76
Xe-Kr	*75*	9	0.61	0.53	0.46	0.71	0.84
Xe-A	*75*	9	1.84	0.56	1.80	1.22	1.36
Kr-A	*76*	8	0.54	0.54	0.56	0.64	0.80
Kr-Ne	*76*	9	2.21	4.77	5.00	6.67	5.21
A-Ne	*77, 81*	30	0.73	4.32	1.23	0.92	0.97
N_2-CO_2	*29, 47*	13	2.31	3.28	1.32	1.51	1.81
C_2H_6-C_2H_4	*56*	12	1.25	1.29	1.34	0.24	0.30
CH_4-C_2H_6	*85*	20	1.01	0.90	0.99	0.30	0.70
C_2H_6-C_3H_6	*56*	9	0.32	0.29	0.38	0.20	0.23
C_3H_8-C_3H_6	*85*	12	0.69	0.72	0.69	1.43	1.64
C_2H_6-C_3H_8	*85*	12	1.71	2.05	1.63	0.46	2.50
CH_4-C_3H_8	*56, 85*	26	2.77	3.13	2.71	0.44	0.57
C_3H_8-CO_2	*82*	16	3.53	1.84	2.50	1.80	2.50
C_2H_4-O_2	*84*	15	4.24	4.75	4.50	0.66	4.21
C_2H_4-N_2	*84*	24	1.27	3.44	1.57	0.85	2.82
C_2H_4-CO	*84*	24	2.42	4.76	2.88	0.75	1.84
CH_4-CO_2	*39*	12	3.42	3.68	3.23	0.71	2.00
CH_4-N_2	*29*	3	2.61	2.08	2.77	6.36	7.45

Table 2. Comparison between Calculated and Experimental Viscosities for Multicomponent Mixtures at Moderate Pressures

System	Reference	Number of points	Average deviation for method of the study
Industrial gases (CO_2, O_2, CO, H_2, N_2)	*67*	24	2.66%
CO_2-O_2-N_2	*46*	20	1.51
Natural gases (CH_4, C_2H_6, N_2, CO_2, O_2)	*4*	25	4.16
Industrial gases (CO_2, O_2, CO, H_2, CH_4, N_2)	*32*	7	2.22
N_2-CO_2-O_2-CO-A	*90*	65	1.69
Natural gas (CH_4, C_2H_6, C_3H_8, N_2)	*56*	6	2.87
Natural gas (CH_4, C_2H_6, C_3H_8, N_2)	*17*	9	0.96
Air	*	489	1.00

* Sources of air data: *2, 3, 8, 9, 10, 11, 12, 23, 25, 27, 28, 30, 31, 36, 37, 38, 41, 44, 46, 47, 48, 53, 54, 61, 62, 64, 68, 69, 73, 78, 79, 80, 83, 86, 88, 92, 95.*

The pseudocritical pressure of the mixture is then calculated from Equations (5), (9), and (10), with $P_{cm} = \frac{z_{cm}RT_{cm}}{V_{cm}}$. From a theoretical standpoint, Leland and Mueller (*52*) have shown that no one set of relationships is rigorously applicable for the estimation of pseudocritical constants over a wide range of temperatures and pressures.

In the present study, very similar conclusions have been reached concerning the pseudocritical constants necessary for the calculation of viscosity values for nonpolar gas mixtures at moderate pressures. In order to establish the appropriate method for the determination of pseudocritical constants, the following relationships were utilized:

$$\mu^*\xi = 34.0 \times 10^{-5}\, T_R^{8/9}, \quad T_R < 1.5 \tag{11}$$

$$\mu^*\xi = 166.8 \times 10^{-5}\, [0.1338\, T_R - 0.0932]^{5/9}, \quad \text{for } T_R \geqq 1.5 \tag{12}$$

$$\text{where } \xi \text{ for mixtures} = \frac{T_{cm}^{1/6}}{(\sum_i x_i\, M_i)^{1/2} P_{cm}^{2/3}}$$

Equations (11) and (12), which are based on very accurate data for argon, were found to represent the viscosity behavior of most nonpolar substances slightly more accurately than the similar equations presented by Stiel and Thodos (*71*).

TREATMENT OF EXPERIMENTAL DATA

A comprehensive literature survey was conducted to obtain the available experimental viscosity data for nonpolar binary gas mixtures at moderate pressures. The components included monatomic and diatomic gases, hydrocarbons, and carbon dioxide. Mixtures containing hydrogen and helium was not included, since these substances possess sizable quantum effects and, therefore, their viscosity behavior cannot be determined from Equations (11) and (12). The mixtures considered are listed in Table 1 along with the sources of the experimental data.

For each experimental composition, sets of ξ and T_{cm} values were calculated by Kay's method, Joffee's method, and the method of Prausnitz and Gunn. Each set of ξ and T_{cm} values was then used to calculate viscosities from Equations (11) and (12). The average deviations between the calculated viscosities and the corresponding experimental values for each pseudocritical method are presented in Table 1. For the 339 experimental points included in the comparisons, the overall average was 2.40% with pseudocritical constants calculated by Kay's method, 1.77% by Joffee's method, and 1.70% by the method of Prausnitz and Gunn. Since the method of Prausnitz and Gunn is more accurate for the calculation of viscosities than Kay's equations and much simpler in application than Joffee's method, this procedure was adopted for use in the later phases of this investigation. Because this method for the establishment of pseudocritical constants enables the calculation of viscosity values to within the average experimental error, it appears that a more elaborate procedure, such as that proposed by Leland and Mueller (*52*), is not required for most nonpolar mixtures.

In Figure 1, a composite curve relating $\mu^*\xi$ to T_R is presented for all the mixtures considered in this study, with ξ and T_{cm} values calculated by the method of Prausnitz and Gunn. The curve of Figure 1 is essentially identical to the relationships presented in Equations (11) and (12) and indicates that for nonpolar gas mixtures (as for pure nonpolar gases) $\mu^*\xi$ is dependent only on the reduced temperature, independent of the critical compressibility factors of the components. When plotted in this manner the data of Rietveld and Van Itterbeek (*65*) for argon-neon mixtures, of Thornton (*75*) for xenon-neon mixtures, of Adzumi (*1*) for mixtures of acetylene with propane and methane, and of Jackson (*39*) for argon-ethylene mixtures showed significant composition effects that were not present with the other mixtures for which the pseudocritical constants effectively corrected for changes in composition. Since in every case data for the same or a similar mixture were available which followed the consistent behavior illustrated in Figure 1, these deviations could not be attributed to the pseudocritical method employed. Therefore, the data that exhibited this abnormal behavior were eliminated from this study. The relationship of Figure 1 in the high temperature region is based on the data of Bonilla, Brooks, and Walker (*9*) for air at temperatures to 2,500°K. Equations (11) and (12) are applicable for temperatures up to approximately 3,000°K., at which point dissociation effects become significant.

For each experimental point, viscosity values were also calculated by Wilke's method and by Equation (4). The average deviations between the calculated and experimental values for each method are included in Table 1. It can be seen from Table 1 that both methods are capable of reproducing viscosity values with a high degree of accuracy. For 339 experimental points, the overall average deviation was 1.00% for Equations (1) and (2) and 1.56% for Equation (4). The agreement that resulted for Wilke's method is particularly striking; evidently it is possible to calculate viscosity values from Equations (1) and

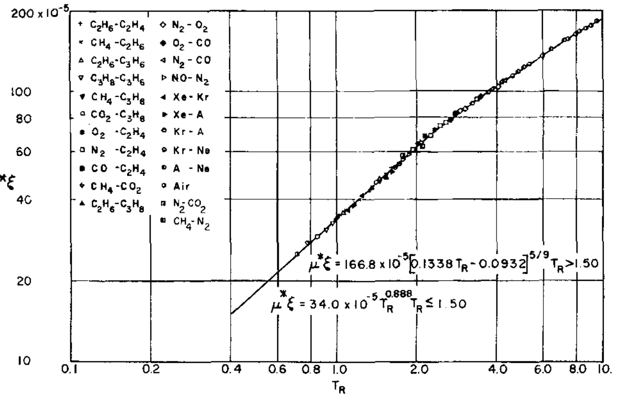

Fig. 1. Relationship between $\mu^*\xi$ and T_R for nonpolar gas mixtures at moderate pressures.

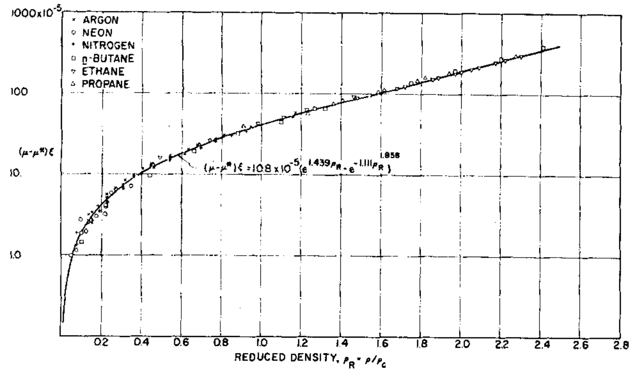

Fig. 2. Relationship between $(\mu\text{-}\mu^*)\xi$ and ρ_R for pure substances.

(2) with better accuracy than can be obtained for the pure component viscosities required by the equations. For several mixtures the graphical analysis of the data revealed that the average deviations resulting from Equations (1) and (2) were less than the experimental error of the data.

For the eight multicomponent mixtures listed in Table 2, including several natural gases, industrial gases, and air treated as a four-component mixture, viscosity values were calculated from Equations (11) and (12) with pseudocritical constants obtained from Equations (5), (9), and (10). Mixtures containing greater than 5% hydrogen could not be included. For multicomponent mixtures this approach is much simpler for the calculation of viscosities than either Wilke's method or Equation (4). The average deviation resulting for each multicomponent mixture is listed in Table 2. For both binary and multicomponent mixtures, the overall average deviation for the method developed in this study is 1.44% for 984 experimental points.

THE VISCOSITY OF GASEOUS MIXTURES AT HIGH PRESSURES

Through semitheoretical considerations, Predvoditelev (*60*) has shown that the residual viscosity, $\mu - \mu^*$, of a dense gas should be a function of the density. Thodos and co-workers (*72*) have used the residual viscosity concept to develop correlations between μ_R, T_R, and P_R for a number of individual substances. By the use of dimensional analysis and available experimental data, Jossi, Stiel, and Thodos (*42*) have developed generalized relationships between the group $(\mu - \mu^*)\xi$ and ρ_R for pure nonpolar substances. Since in a number of recent experimental investigations the residual viscosity concept has also been found to be applicable for gaseous mixtures, an approach similar to that followed by Jossi, Stiel, and Thodos has been employed in the present study.

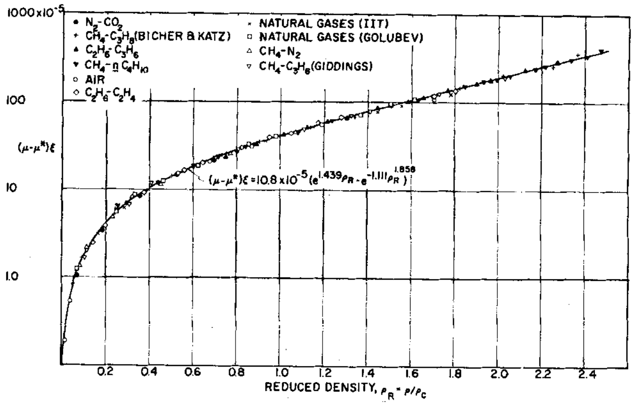

Fig. 3. Relationship between $(\mu\text{-}\mu^*)\xi$ and ρ_R for nonpolar mixtures.

Very accurate viscosity data have recently appeared in the literature for argon, nitrogen, and neon (*24*), and for the light hydrocarbons ethane (*22*), propane (*70*), and *n*-butane (*20*), which were not available at the time the study of Jossi et al. was conducted. Since an accurate relationship between $(\mu - \mu^*)\xi$ and ρ_R must be available to permit the calculation of the viscosity of dense gaseous mixtures with the pseudocritical constants of the mixture, the results of the previous study were tested with the new data. Values of $(\mu - \mu^*)\xi$ obtained from these data were plotted against ρ_R, as shown in Figure 2. A smooth curve resulted, which is essentially identical to the relationship presented by Jossi, Stiel, and Thodos. The relationship of Figure 2 was expressed in the following manner, in a modification of a form originally suggested by Eakin (*21*)

$$(\mu - \mu^*)\xi = 10.8 \times 10^{-5} (e^{1.439\rho_R} - e^{-1.111\rho_R^{1.858}}) \qquad (13)$$

The data of Flynn, Hanks, and Ross (*24*) for argon, neon, and nitrogen, which are claimed to be accurate to within 0.1%, confirm the general validity of the residual viscosity concept. For the eighty experimental points presented by these investigators, Equation (13) reproduced the data with an average deviation of 1.05%. In addition, viscosities calculated with Equation (13) showed an average deviation of 1.59% for the 47 experimental values of ethane (*22*) and of 3.30% for fifty-eight experimental propane (*70*) and *n*-butane (*20*) viscosities in the dense gaseous region. Therefore, Equation (13) was chosen to form the basis of the method developed in this study for the calculation of viscosity values for gaseous mixtures.

Viscosity data available in the literature for nine binary and multicomponent mixtures, including air, natural gases, hydrocarbon mixtures, and mixtures of nitrogen with methane and carbon dioxide, were used in conjunction with pseudocritical constants obtained from Equations (5), (9), and (10) and calculated values of μ^* to obtain $(\mu - \mu^*)\xi$ values for each experimental point. The mix-

Table 3. Sources of Viscosity and Density Data and Average Deviations for Dense Gaseous Mixtures

System	Reference	Number of points	Temperature range, °K.	Pressure range, atm.	Average deviation	Source of PVT data
C_2H_6-C_2H_4	*56*	144	323-473	20-600	4.51%	*58*
CH_4-N_2	*29*	15	293-373	20-300	2.20	*58*
CO_2-N_2	*29*	30	287-374	20-240	1.21	*50, 58*
Natural Gas	*56*	98	273-523	20-450	3.44	*58*
Natural Gas	*17*	110	295-398	5-682	5.90	*17*
CH_4-C_3H_8	*5*	169	298-498	27-341	6.20	*5, 63*
CH_4-C_3H_8	*26*	314	311-413	8-548	2.52	*66*
C_2H_6-C_3H_6	*56*	126	373-473	20-600	5.87	*55*
CH_4-*n* C_4H_{10}	*20*	104	273-478	10-550	4.14	*19*
Air	*6, 28, 38, 45, 47, 48, 54, 57*	286	273-543	5-775	1.71	*6, 16, 33, 47*

tures are listed in Table 3 along with the sources of the viscosity data and the range of temperatures and pressures involved. A tabulation of the data utilized is available on request from the Department of Chemical Engineering and Metallurgy, Syracuse University. In Figure 3 a composite curve between $(\mu - \mu^*)\xi$ and reduced density is presented for each mixture. The sources of the density values, which were obtained from experimental data or from the accurate correlation presented by Pitzer et al. (*58*) with the use of the pseudocritical constants of the mixture (*59*), are also included in Table 3. The pseudocritical density of the mixture is obtained from Equation (9) as $\rho_{cm} = \dfrac{\sum_i x_i M_i}{\sum_i x_i V_{c_i}}$. The curve of Figure 3 for mixtures is essentially identical to that of Figure 2 for pure components and is therefore represented by Equation (13).

For the nine mixtures included in Figure 2, viscosity values were calculated from Equation (13) with μ^* values obtained from Equations (11) or (12) and pseudocritical constants resulting from Equations (5), (9), and (10). In order to simplify these calculations, Equation (13) was programmed on an IBM 7070 computer and the results tabulated for even intervals of ρ_R. Copies of the tabulated values are available on request from the Department of Chemical Engineering and Metallurgy, Syracuse University. For 1,396 points, the overall average deviation was found to be 3.73%. In view of the wide range of temperature and pressure involved, the experimental errors inherent in the determination of viscosity values for mixtures at high pressures, the fact that the density values were found to be reproducible only to within 2%, and the empirical nature of the pseudocritical rules utilized, this agreement is considered to be very reasonable. The average deviation for each mixture is also included in Table 3. For several mixtures the experimental viscosity data for certain ranges of temperature or density did not follow the consistent behavior exhibited in Figure 3. These anomalous data are listed as follows:

Mixture	Range
CH_4—C_3H_8 (*5*)	$\rho_R \geqq 1.2$
C_2H_6—C_3H_6 (*56*)	$\rho_R \leqq 1.0$
C_2H_6—C_2H_4 (*56*)	$T = 323$°K.
Natural gas (*56*)	$T = 273$°K.
Natural gas (*17*)	$\rho_R \geqq 1.6$
Air (*54*)	$\rho_R \geqq 1.25$, $T = 423$°K., 473°K.

If these data are removed from consideration, the overall average deviation for the remaining 1,188 points is only 2.63%. Lee, Starling, Dolan, and Ellington (*51*) also obtained significant deviations for the methane-propane data (*5*) at high pressures.

Prausnitz and Gunn (*59*) suggest that their pseudocritical rules are best for mixtures of substances whose critical volumes and critical temperatures are similar, and for reduced temperatures greater than 1.3. In the present study, for no mixture did the critical properties of the components vary enough so that the errors encountered were considered to be due to the pseudocritical method utilized. However, Equations (11), (12), and (13) are independent of the method used to calculate the pseudocritical constants of the mixture, and, therefore, if a more accurate method is developed or if mixtures are treated for which the Prausnitz-Gunn rules do not hold, the procedure recommended in this study can be easily modified. Giddings (*26*) utilized an approach similar to that advanced in this study to correlate his experimental data for the methane-propane system by the use of the pseudocritical method presented by Leland and Mueller (*52*). However, for these data the use of pseudocritical constants calculated from Equations (5), (9), and (10) was found to lead to less errors in the calculation of viscosities from Equation (13).

For several of the mixtures considered in this study, including the methane-*n*-butane and methane-propane systems, the temperature and pressure range included the liquid region. However, the relationship of Equation (13) is not really applicable to liquids for ρ_R greater than 2.0, since it has been established experimentally (*94*) that the viscosity of a liquid at higher reduced densities depends on both density and temperature. In addition, the pseudocritical rules employed have not been tested for the liquid region. Therefore, the accuracy of Equation (13) is not considered to be as good for the liquid region as for the dense gaseous region. For pure substances, errors greater than 10% were encountered for propane (*70*) and *n*-butane (*20*) at high densities with the use of Equation (13).

For mixtures for which experimental data are not available, accurate density values can usually be obtained from the tables of Pitzer et al. (*58*) by the use of pseudocritical constants obtained from Equations (5), (9), and (10). The acentric factor of the mixture is estimated as a linear combination of the acentric factors of the pure components (*59*).

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NOTATION

A, B = functions in Equations (9) and (10)
A^* = ratio of the reduced collision integrals for viscosity and diffusivity at atmospheric pressure
D_{ik} = binary diffusion coefficient, sq. cm./sec.
M = molecular weight
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 82.05 atm. cc./g.-mole °K.
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
V = volume, cc./g.-mole
V_c = critical volume, cc./g.-mole
x = mole fraction
z = compressibility factor

Greek Letters

μ = viscosity, centipoises
μ^* = viscosity at moderate pressures (0.2 to 5 atm.), centipoises
μ_c = viscosity at the critical point, centipoises
ξ = viscosity parameter, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
π = constant, 3.1416
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
ψ = parameter in Equation (1)
ω = acentric factor
$\Omega^{(2,2)*}$ = reduced collision integral for viscosity
$\Omega^{(1,1)*}$ = reduced collision integral for diffusivity

Subscripts

i, k = components i and k of a mixture
ik = property characteristic of interactions between molecules of species i and molecules of species k

1, 2 = components 1 and 2 of a binary mixture
m = pseudocritical property of a mixture

LITERATURE CITED

1. Adzumi, Hiroshi, *Bull. Chem. Soc. Japan*, **12**, 199 (1937).
2. Banerjea, G. B., and Plattanik, B., *Z. Phys.*, **110**, 676 (1938).
3. Bearden, J. A., *Phys. Rev.*, **56**, 1023 (1939).
4. Berwald, W. B., and T. W. Johnson, *U. S. Bureau of Mines Tech. Paper No. 555* (1933).
5. Bicher, L. B., and D. L. Katz, *Ind. Eng. Chem.*, **35**, 754 (1943).
6. Biles, M. B., and J. A. Putnam, *Natl. Advisory Comm. Aeronaut. Tech. Note 2783* (1952).
7. Bird, R. B., and J. R. Brock, *A.I.Ch.E. Journal*, **5**, 436 (1959).
8. Bond, W. N., *Nature*, **137**, 1031 (1936).
9. Bonilla, C. F., R. D. Brooks, and P. L. Walker, *Proc. General Disc. Heat Transfer II*, Inst. Mech. Engr. London, 167 (1951).
10. Braune, H. R. Basch, and W. Wentzel, *Z. Phys. Chem.*, **A137**, 176 (1928).
11. Breitenbach, Paul, *Ann. Phys.*, **67**, 803 (1899).
12. Bremond, Pierre, *Compt. Rend.*, **196**, 1472 (1933).
13. Brokaw, R. S., *J. Chem. Phys.*, **29**, 391 (1958).
14. ———, *Natl. Aeronaut. Space Admin. Tech. Rept. R-81* (1961).
15. Buddenberg, J. W., and C. R. Wilke, *Ind. Eng. Chem.*, **41**, 1345 (1949).
16. Byrne, Robert, and George Thodos, *A.I.Ch.E. Journal*, **7**, 185 (1961).
17. Carr, N. L., *Bull. Inst. Gas Technol.*, **23** (1953).
18. Comings, E. W., B. J. Mayland, and R. S. Egly, *Univ. of Illinois Engr. Exp. Sta. Bull.*, **42**, No. 15 (1944).
19. Dean, David E., M.S. thesis, Syracuse Univ., Syracuse, New York (1964).
20. Dolan, J. P., M.S. thesis, Illinois Inst. Technol., Chicago, Illinois (1962).
21. Eakin, B. E., Ph.D. dissertation, Illinois Inst. Technol., Chicago, Illinois (1962).
22. ———, K. E. Starling, J. P. Dolan, and R. T. Ellington, *J. Chem. Engr. Data*, **7**, 33 (1962).
23. Edwards, R. S., and A. O. Rankine, *Proc. Roy. Soc. (London)*, **117A**, 245 (1927).
24. Flynn, G. P., R. V. Hanks, N. A. LeMaire, and J. Ross, *J. Chem. Phys.*, **38**, 154 (1963).
25. Fortier, Andre, *Compt. Rend.*, **208**, 506 (1939).
26. Giddings, J. G., Ph.D. dissertation, Rice Univ., Houston, Texas (1963).
27. Gilchrist, Lachlan, *Phys. Rev.*, **1**, 124 (1913).
28. Golubev, I. F., *J. Tech. Phys. (USSR)*, **8**, 1932 (1938).
29. ———, and V. A. Petrov, *Tr. Gos. Nauch-Issl. Proekt. Inst. Azot. Prom.*, **7**, No. 1 (1953).
30. Gridley, J. H., and A. H. Gibson, *Proc. Roy. Soc. (London)*, **80A**, 114 (1908).
31. Harrington, E. L., *Phys. Rev.*, **55**, 230 (1939).
32. Herning, F., and L. Zipperer, *Gas Wasserfach*, **79**, 49 (1936).
33. Hilsenrath, Joseph, *NBS Circular 564* (1955).
34. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
35. ———, M. H. Taylor, Taro Kihara, and Reginald Rutherford, *Phys. Fluids*, **4**, 663 (1961).
36. Hogg, J. L., *Proc. Am. Acad. Art. Sci.*, **40**, 611 (1905).
37. Houston, W. V., *Phys. Rev.*, **52**, 751 (1937).
38. Iwasaki, Hiroji, *Sci. Rept. Res. Inst., Tohoku Univ.*, **3A**, 247 (1961).
39. Jackson, W. M., *J. Phys. Chem.*, **60**, 789 (1956).
40. Joffe, J., *Ind. Eng. Chem.*, **39**, 837 (1947).
41. Johnston, H. L., and K. E. McCloskey, *J. Phys. Chem.*, **44**, 1038 (1939).
42. Jossi, J. A., L. I. Stiel, and George Thodos, *A.I.Ch.E. Journal*, **8**, 59 (1962).
43. Kay, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).
44. Kellstrom, Gunnar, *Nature*, **136**, 682 (1935).
45. ———, *Arkiv. Matematik Astron. Phys.*, **27A**, 1 (1941).
46. Kenney, M. J., R. J. Sarjant, and M. W. Thring, *Brit. J. Appl. Phys.*, **7**, 324 (1956).
47. Kestin, Joseph, and Wolfgang Leidenfrost, *Physica*, **25**, 525 (1959).
48. ———, and H. E. Wang, *Trans. Am. Soc. Mech. Engrs.*, **80**, 11 (1958).
49. Kleint, F., *Verhandel. Deut. Phys. Ges.*, **7**, 146 (1905).
50. Kritschewsky, I. R., and V. P. Markov, *Acta Physicochim.*, **12**, 62 (1940).
51. Lee, A. L., K. E. Starling, J. P. Dolan, and R. T. Ellington, *A.I.Ch.E. Journal*, **10**, 694 (1964).
52. Leland, T. W., and W. H. Mueller, *Ind. Eng. Chem.*, **51**, 597 (1959).
53. Ling, T. D., and Matthew Van Winkle, *J. Chem. Eng. Data*, **3**, 82 (1958).
54. Makita, Tadashi, *J. Soc. High Pressure Gas Ind.*, **23**, 367 (1959).
55. McKay, R. A., H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43**, 2112 (1951).
56. Meshcheryakov, N. V., and I. F. Golubev, *Tr. Gos. Nauch-Issl. Proekst. Inst. Azot. Prom.*, **27**, No. 3 (1954).
57. Nasini, A. G., and G. Pastonesi, *Gazz. Chim. Ital.*, **63**, 821 (1933).
58. Pitzer, K. S., D. Z. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Peterson, *J. Am. Chem. Soc.*, **77**, 3427 (1955).
59. Prausnitz, J. M., and R. D. Gunn, *A.I.Ch.E. Journal*, **4**, 432 (1955).
60. Predvoditelev, A. S., *J. Phys. Chem. (U.S.S.R.)*, **22**, 339 (1948).
61. Rankine, A. O., *Proc. Roy. Soc. (London)*, **84A**, 181 (1910).
62. Rapp, I. M., *Phys. Rev.*, **2**, 363 (1913).
63. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950).
64. Rigden, P. J., *Philos. Mag.*, **25**, 961 (1938).
65. Rietveld, A. O., and A. van Itterbeek, *Physica*, **22**, 785 (1956).
66. Sage, B. H., and W. N. Lacey, "API Research Project 37," American Petroleum Institute, New York (1950).
67. Schmid, C., *Gas Wasserfach*, **85**, 92 (1942).
68. Schultze, Hugo, *Ann. Phys.*, **5**, 140 (1901).
69. Shilling, W. G., and A. E. Laxton, *Philos. Mag.*, **10**, 721 (1930).
70. Starling, K. E., B. E. Eakin, and R. T. Ellington, *A.I.Ch.E. Journal*, **6**, 438 (1960).
71. Stiel, L. I., and George Thodos, *A.I.Ch.E. Journal*, **7**, 611 (1961).
72. ————, "Progress in International Research on Thermodynamic and Transport Properties," pp. 352-365, Am. Soc. Mech. Engrs., New York (1962).
73. Sutherland, B. P., and Otto Maass, *Can. J. Res.*, **6**, 428 (1932).
74. Sutherland, William, *Philos. Mag.*, **40**, 421 (1895).
75. Thornton, E., *Proc. Phys. Soc. (London)*, **76**, 104 (1960).
76. ———, *ibid.*, **77**, 1166 (1961).
77. ———, "Progress in International Research on Thermodynamic and Transport Properties," pp. 527-529, Am. Soc. Chem. Engrs., New York (1962).
78. Titani, Toshizo, *Bull. Chem. Soc. Japan*, **4**, 277 (1929).
79. ———, *ibid.*, **8**, 255 (1933).
80. Tomlinson, H., *Philos. Trans. Roy. Soc. (London)*, **177A**, 767 (1886).
81. Trautz, Max, and H. E. Binkele, *Ann. Phys.*, **5**, No. 5, 561 (1930).
82. ———, and Frederich Kurz, *ibid.*, **82**, 227 (1927).
83. ———, and Walter Ludewigs, *ibid.*, **3**, No. 5, 409 (1929).
84. ———, and Albert Malster, *ibid.*, **7**, 409 (1930).
85. ———, and K. G. Sorg, *ibid.*, **10**, 81 (1931).
86. ———, and Robert Zink, *ibid.*, **7**, No. 5, 427 (1930).
87. Uyehara, O. A., and K. M. Watson, *Natl. Petrol. News Tech. Sec.*, **36**, 714 (1944).
88. Van Dyke, K. S., *Phys. Rev.*, **21**, 250 (1923).
89. Vasilesco, Virgile, *Ann. Phys.*, **20**, 137 (1945).
90. Westmoreland, J. C., *Natl. Advisory Comm. Aeronaut. Tech. Note 3180* (1954).
91. Wilke, C. R., *J. Chem. Phys.*, **18**, 517 (1950).

92. Williams, F. A., *Proc. Roy. Soc. (London)*, **110A**, 141 (1926).
93. Wright, P. G., and Peter Gray, *Trans. Faraday Soc.*, **58**, 1 (1962).
94. Zhdanova, N. F., *Sov. Phys. JETP*, **4**, 749 (1957).
95. Zipperer, L., and G. Muller, *Gas Wasserfach*, **75**, 623 (1932).

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An Analytical Solution for the Nonlinear Frequency Response of Radiant Heat Transfer

EDWARD H. BLUM
Princeton University, Princeton, New Jersey

An analytical solution is presented for the nonlinear frequency response of a system in which radiant heat transfer is coupled with conduction. The model is that of an object inside an evacuated enclosure whose wall temperature oscillates about a mean. A perturbation analysis solves the describing equations for oscillatory amplitudes less than one-tenth the mean wall temperature. An exact solution to a Ricatti differential equation verifies the perturbation analysis. These solutions show that, contrary to linear experience, the average object temperature over an oscillatory cycle exceeds the mean at the wall.

The complete solution for the frequency response can be divided into three regimes. In the first, at low frequencies, all response is truly linear. In the second, higher harmonics become important, but the response remains that of a lumped parameter system. In the third, response changes with distance from the object surface and the response at the surface dominates. Nonlinearities are important in the second and third regimes. The solution has several applications.

In many processes thermal radiation forms a significant part of the total energy transfer. Yet the response of thermal radiation to temperature changes is not well understood because the equations describing radiant heat transfer are fundamentally nonlinear. This paper analyzes the nonlinear response of radiant heat transfer to temperature oscillations, and describes the response in detail. Some unusual and unexpected results are obtained.

Radiant heat transfer is particularly important in furnaces, high-temperature processes, and in evacuated or low-pressure systems such as outer space. In general, wherever the temperature is high so that the radiant heat flux is substantial, or the pressure is low so that convection is negligible, radiant heat transfer will be significant. Anywhere radiant heat transfer is important and the temperature changes, the dynamic response will be of interest.

A consequence of quantum statistics is that the heat flux in radiant transfer varies as the fourth power of the absolute temperature (*11*). Thus in systems where radiant heat transfer is important, the differential equations describing temperature changes are nonlinear. In general, because of the dominant fourth-power nonlinearity, these differential equations cannot be solved in closed form.

In radiant heat transfer systems where the effects of convection and conduction are both negligible, the dynamic response is described by a first-order ordinary differential equation containing a nonlinear term. This equation can be solved exactly for a few simple cases, and numerical solutions can be obtained by conventional methods.

When conduction as well as radiation becomes important, however, the system is described by the heat conduction equation with a linear flux boundary condition on one surface and a nonlinear flux boundary condition on the other. No complete exact solutions are known for the heat conduction equation when one of its boundary conditions is nonlinear and time varying and numerical solutions are generally difficult to obtain. Even when numerical solutions can be achieved, the information they contain is highly restricted. It is difficult to extrapolate the solutions with confidence to slightly different systems, and the physical insight one attains is usually minimal.

A number of approximate solutions to problems involving both conduction and radiation have been obtained (*1, 3, 7, 10*). These solutions are in general quite complex and restricted to particular problems. They thus do not afford the broad intuitive understanding of the interaction of radiant and conductive heat transfer that is required for engineering analysis and design.

Faced with a similar inadequacy of particular numerical solutions or complex approximations, one often characterizes a linear system by its steady state response to a forced sinusoidal input. The frequency response, as this characterization is called, furnishes a "fingerprint" of the system, and affords a basis from which the response to different inputs may be determined. Since radiant heat transfer is nonlinear, and the superposition principle does not hold, the frequency response is not so valuable quantitatively as it is for linear systems. Nevertheless, the frequency response of radiant heat transfer does yield considerable qualitative information and intuitive understanding.

PHYSICAL MODEL AND ASSUMPTIONS

The physical model, as shown in Figure 1, consists of a homogeneous slab in an evacuated enclosure where the