Viscosity of Nonpolar Gaseous Mixtures at Normal Pressures

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The relationship between $\mu^*\xi$ and T_R for nonpolar gases at normal pressures is used to predict the viscosity for their mixtures. For such mixtures, pseudocritical temperatures are used to obtain T_R. To establish ξ_m for a mixture, a binary interaction model has been applied that utilizes composition and the ξ values of the pure components.

Viscosities have been calculated for twenty binary systems which include helium and hydrogen. These calculated values produce an average deviation of 1.97% for 148 compositions. This method was also applied to the helium-neon-argon ternary system at 100°C. to obtain for four mixtures examined an average deviation of 2.2%.

Several methods for the prediction of viscosity of gaseous mixtures at essentially atmospheric pressure have appeared in the literature. Noteworthy of mention are those proposed by Sutherland (*9*), Wilke (*17*), and Curtiss and Hirschfelder (*1*).

For pure gases at nearly atmospheric pressure, Stiel and Thodos (*8*), utilizing a dimensional analysis, show that viscosity is a unique function of T_R and the system parameters ξ and z_c as follows:

$$\mu^*\xi = f(z_c, T_R) \qquad (1)$$

A comparison of viscosities of several nonpolar gases indicates that $\mu^*\xi$ is independent of z_c and that this product is a function of T_R only. With the exception of hydrogen and helium, their study based on fifty nonpolar substances, including monatomic, diatomic, and polyatomic gases, produced a single relationship which can be expressed in equation form as follows:

$$\mu^*\xi \times 10^5 = 46.10 T_R^{0.618} - 20.4 e^{-0.449 T_R} + 19.4 e^{-4.058 T_R} + 1 \quad \text{(nonpolar gases)} \qquad (2)$$

For hydrogen and helium, the specific relationships were found to be

$$\mu^*\xi \times 10^5 = 47.65 T_R^{0.657} - 20 e^{-0.858 T_R} + 19 e^{-3.995 T_R} + 1 \quad \text{(hydrogen)} \qquad (3)$$

$$\mu^*\xi \times 10^5 = 52.57 T_R^{0.656} - 18.9 e^{-1.144 T_R} + 17.9 e^{-5.182 T_R} + 1 \quad \text{(helium)} \qquad (4)$$

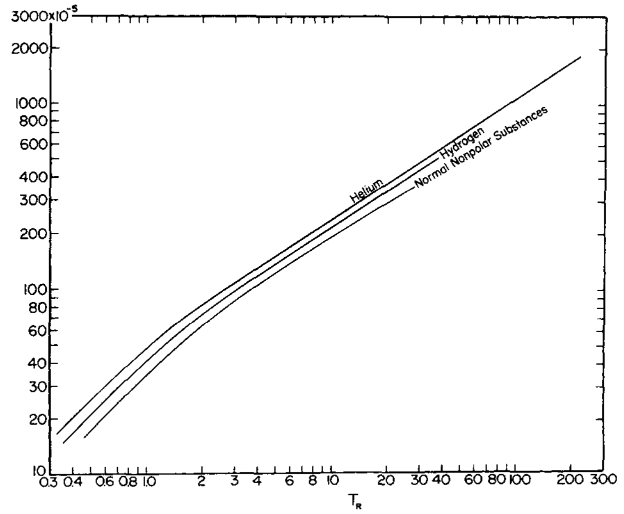


Fig. 1. Relationships of $\mu^*\xi$ vs. T_R for nonpolar gases at moderate pressures.

Equations (2), (3), and (4) were derived from the relationships of Figure 1, developed by Stiel and Thodos (*8*). Dean and Stiel (*2*), utilizing viscosities for nonpolar gaseous mixtures and the pseudocritical constants of Prausnitz and Gunn (*5*), establish a relationship of $\mu^*\xi_m$ vs. T_R that is nearly the same to that represented by Equation (2).

In this investigation an attempt is made to establish ξ_m, the viscosity parameter for a mixture, from the pure component values ξ in place of pseudocritical constants. This approach should offer a means for the establishment of this viscosity parameter for mixtures that bears directly on the composition of the mixture and not on its pseudocritical constants.

TREATMENT OF EXPERIMENTAL DATA

Viscosity measurements available in the literature for a number of binary systems were considered. These systems, including several which contain helium and hydrogen, along with the viscosity parameter of each component and sources of viscosity data of their mixtures are presented in Table 1. In Figure 2 are presented the viscosity measurements of Trautz and Melster (*14*) for the hydrogen-oxygen system at atmospheric pressure and temperatures of 26.9°, 126.9°, 226.9°, and 276.9°C. To establish for this binary system values of the viscosity parameter $\mu^*\xi_m$,

TABLE 1. BINARY SYSTEMS INVESTIGATED AND VISCOSITY PARAMETERS OF THEIR COMPONENTS

System i — j	ξ_i	ξ_j	Sources of viscosity data
He—Ne	0.381	0.0466	12
He—A	0.381	0.0276	12
He—Kr	0.381	0.0184	11
H_2—Ne	0.230	0.0466	12
H_2—CH_4	0.230	0.0464	15
H_2—C_3H_8	0.230	0.0334	13
H_2—O_2	0.230	0.0301	14
H_2—A	0.230	0.0276	12
H_2—CO_2	0.230	0.0224	12
Ne—A	0.0466	0.0276	6
Ne—Kr	0.0466	0.0184	11
N_2—CO	0.0407	0.0402	14
CO—C_2H_4	0.0402	0.0356	14
N_2—C_2H_4	0.0407	0.0356	14
C_2H_4—O_2	0.0356	0.0301	14
A—Kr	0.0276	0.0184	11
CO—O_2	0.0402	0.0301	14
N_2—O_2	0.0407	0.0301	14
C_3H_8—CO_2	0.0334	0.0224	13
CH_4—C_3H_8	0.0464	0.0334	15

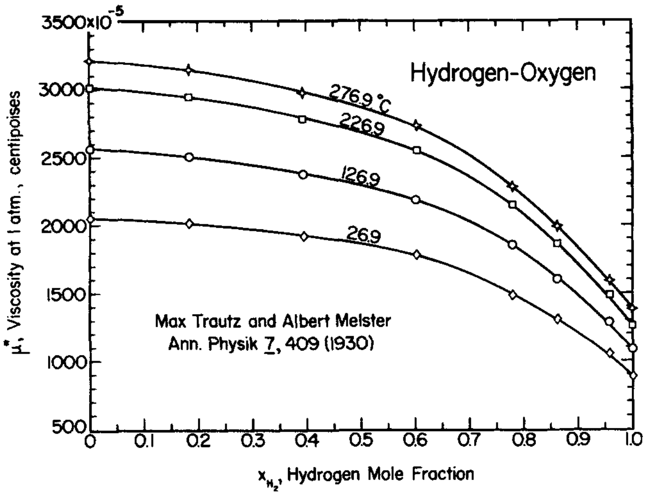


Fig. 2. Viscosity-composition relationships for the hydrogen-oxygen system at atmospheric pressure and 26.9°, 126.9°, 226.9°, and 276.9°C.

the $\mu^*\xi$ vs. T_R relationships for pure substances presented in Figure 1 were assumed to apply.

Thus, for each isotherm of the hydrogen-oxygen system, it became necessary to locate a point on the hydrogen curve and a corresponding point for oxygen on the curve representing the normal nonpolar gases. A straight line connecting these two points was assumed to represent for this particular isotherm the $\mu^*\xi_m$ vs. T_R behavior of this system. In this connection, the pseudocritical temperature of Kay (*3*) was used to obtain T_R' values for each respective mixture. These pseudoreduced temperatures made possible the establishment of $\mu^*\xi_m$ values from the linear interpolation, and the corresponding experimental viscosity measurements permitted the establishment of ξ_m for each mixture. This interpolation became necessary because hydrogen does not follow a normal nonpolar viscosity behavior. The same argument applies to helium. Otherwise, for normally behaving substances, the values of $\mu^*\xi_m$ for mixtures follow the basic normal nonpolar relationship of pure substances presented in Figure 1. Table 2 summarizes the viscosity parameters ξ_m for the hydrogen-oxygen system resulting from the viscosity measurements of Trautz and Melster (*14*) at 26.9°, 126.9°, 226.9°, and 276.9°C. These calculated values of ξ_m are found to be essentially independent of temperature, and, consequently, for this system they become a unique function of composition only. For each composition the ξ_m values were averaged and were plotted against hydrogen composition to produce the relationship presented in Figure 3. A similar analysis was followed for the establishment of ξ_m values for all the systems presented in Table 1. For helium containing systems, the approach used was identical to that employed for the hydrogen-oxygen system. If the mixture did not contain hydrogen or helium, the normal nonpolar relationship of Figure 1 represented the behavior of pure substances and mixtures as well.

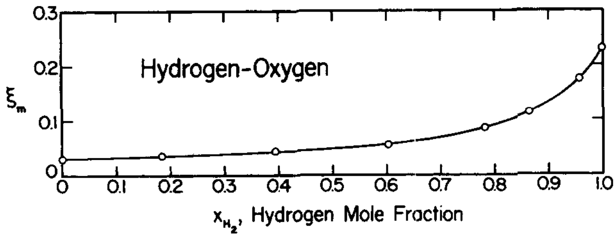


Fig. 3. Relationship between ξ_m and x_{H_2} resulting from the viscosity measurements of the hydrogen-oxygen system at 1 atm. and 26.9°, 126.9°, 226.9°, and 276.9°C.

To generate a functional relationship for the viscosity parameter of mixtures ξ_m, the residual quantity of this parameter $\xi_m - \xi'$ has been related to the corresponding composition of each mixture. This excess quantity represents the departure resulting from dissimilarities of the values of ξ of the components comprising the mixture. Thus, if the viscosity parameters ξ of the two components of a binary mixture are alike, then $\xi_m - \xi'$ becomes zero. Conversely, if these viscosity parameters for these two components depart considerably from each other, then the residual viscosity parameter $\xi_m - \xi'$ becomes significant.

The dependence of $\xi_m - \xi'$ on composition for binary mixtures suggests an interaction model of the form

$$\xi_m - \xi' = \frac{x_i x_j}{A_{ij} + B_{ij}\, x_i} \tag{5}$$

where component i is that having the greater value of ξ, that is, $\xi_i > \xi_j$. For the four temperatures of the hydrogen-oxygen system, a plot of $x_{H_2}x_{O_2}/(\xi_m - \xi')$ against x_{H_2} produced over the complete composition range the linear relationship of Figure 4.

By following an analysis similar to that used for the hydrogen-oxygen system, values of the quantity $x_i x_j/(\xi_m - \xi')$ were plotted against x_i for the binary systems included in this study. The intercepts A_{ij} and slopes B_{ij} of the resulting straight lines are presented for these systems in Table 3. Of the several attempts to correlate the slopes B_{ij} with the viscosity parameters of the pure components, the best resulted when B_{ij} was related to the difference of the viscosity parameters of the pure components $\xi_i - \xi_j$. In this difference, ξ_i represents the higher of the two values $\xi_i > \xi_j$, and therefore $\xi_i - \xi_j$ is always positive. The slopes B_{ij} of all the binary systems included in this study have been plotted against $\xi_i - \xi_j$ on log-log coordinates as shown in Figure 5. The relationship of this figure is essentially linear, has a slope of −1, and an intercept of +1.

TABLE 2. SUMMARY OF CALCULATED VISCOSITY PARAMETERS FOR HYDROGEN-OXYGEN MIXTURES AT DIFFERENT TEMPERATURES

Mole fraction		ξ_m, viscosity parameter for mixtures				
x_{H_2}	x_{O_2}	26.9°C.	126.9°C.	226.9°C.	276.9°C.	Average
0.0000	1.0000	0.0301	0.0300	0.0302	0.0303	0.0302
0.1835	0.8165	0.0347	0.0345	0.0342	0.0343	0.0344
0.3945	0.6055	0.0426	0.0428	0.0430	0.0426	0.0428
0.6030	0.3970	0.0566	0.0570	0.0567	0.0571	0.0568
0.7808	0.2192	0.0857	0.0845	0.0848	0.0852	0.0850
0.8633	0.1367	0.1126	0.1124	0.1125	0.1115	0.1122
0.9586	0.0414	0.1728	0.1716	0.1714	0.1705	0.1716
1.0000	0.0000	0.2283	0.2245	0.2240	0.2136	0.2226

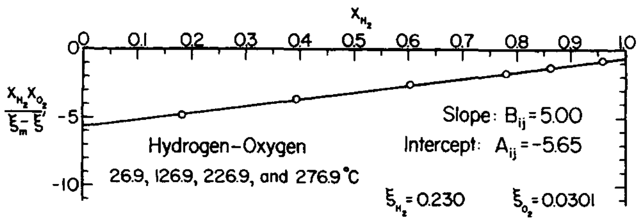


Fig. 4. Relationship between $x_{H_2}\,x_{O_2}/(\xi_m-\xi')$ and x_{H_2} for the hydrogen-oxygen system.

Therefore, the interaction coefficient B_{ij} can be obtained from the relationship

$$B_{ij} = \frac{1}{\xi_i - \xi_j} \tag{6}$$

Equation (6) applies to all types of nonpolar binary systems and is particularly applicable to systems that contain helium and hydrogen. For binary systems not containing these components, some scatter is noted in the low range of $\xi_i - \xi_j$ of Figure 5. This results from the high sensitivity of the parameter difference $\xi_i - \xi_j$, representing these systems in this range.

When the product $A_{ij}B_{ij}$ was plotted against $\xi_i - \xi_j$ on logarithmic coordinates, the linear relationship presented in Figure 6 resulted. This relationship can be expressed in equation form as

$$A_{ij}B_{ij} = -\frac{0.875}{(\xi_i - \xi_j)^{2.18}} \tag{7}$$

and applies to binary helium and hydrogen mixtures. Despite the fact that Equations (6) and (7) were developed from an overall consideration of all types of systems, their application indicates that some deviations in viscosity result for mixtures containing helium and hydrogen. A careful examination indicated that Equation (6) has the capability of reproducing properly the interaction coefficient B_{ij} for all types of systems. However, A_{ij} values calculated with Equation (7) for systems containing helium and hydrogen produced viscosities which did not agree closely with experimental values. This condition necessitated that specific relationships be assigned to helium and hydrogen containing systems. A careful analysis of the information available produced the following relationships for systems containing these two abnormally behaving components:

$$A_{ij}B_{ij} = -\frac{0.500}{(\xi_i - \xi_j)^{2.48}} \quad \text{(hydrogen systems)} \tag{8}$$

$$A_{ij}B_{ij} = -\frac{0.610}{(\xi_i - \xi_j)^{2.48}} \quad \text{(helium systems)} \tag{9}$$

Since the value of B_{ij} represented by Equation (6) is common to all types of nonpolar systems and includes helium and hydrogen, the relationship of this equation can be used to obtain the direct dependence of A_{ij} vs. $\xi_i - \xi_j$ for normal binary systems, hydrogen containing systems, and helium containing systems represented by Equations (7), (8), and (9), respectively.

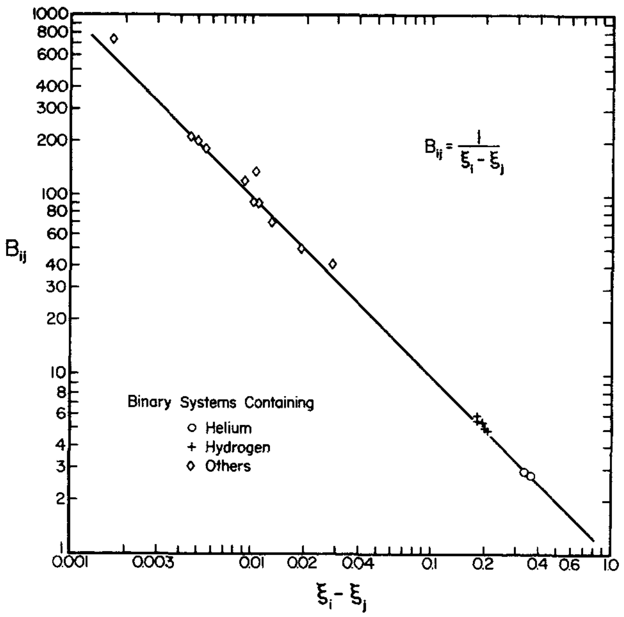


Fig. 5. Relationship between B_{ij} and ξ_i-ξ_j resulting from the nonpolar binary systems included in this study.

EXTENSION TO MULTICOMPONENT SYSTEMS

The method developed for binaries can be extended in application to include systems containing more than two components. In this context T_c', the pseudocritical temperature of the multicomponent system, is first calculated by using the method of Kay (3) in order to establish $\mu^*\xi_m$ from Figure 1. For systems which contain helium and/or hydrogen $\mu^*\xi$ is prorated linearly with composition at the particular reduced temperature. The viscosity parameter for a multicomponent mixture ξ_m can be calculated by using the relationship

$$\xi_m - \xi' = \sum_{i=1}^{k}\sum_{j=1}^{k} \frac{x_i x_j}{A_{ij} + B_{ij}\,x_i} \quad (j > 1) \tag{10}$$

Equation (10) presupposes the existence of only binary interactions as reflected in the coefficients A_{ij} and B_{ij}. In Equation (10), ξ' represents the molar average value of the viscosity parameter of the mixture as follows:

$$\xi' = \sum_{i=1}^{k} \xi_i x_i \tag{11}$$

To illustrate the extension of the method developed for binary systems to multicomponent systems, the following example is presented.

Calculate at 373°K. and atmospheric pressure the viscosity of a mixture having the following composition expressed in mole fraction: $x_{He} = 0.5429$, $x_{Ne} = 0.2189$, and $x_A = 0.2382$.

	x	T_c, °K.	ξ	xT_c	$x\xi$
Helium	0.5429	5.21	0.381	2.8	0.2068
Neon	0.2189	44.5	0.0466	9.7	0.0102
Argon	0.2382	151.2	0.0276	36.0	0.0066
	1.0000			$T_c' = 48.5$°K.	$\xi' = 0.2236$

At 373°K., $T_R' = 373/48.5 = 7.69$. Reference to Figure 1 at this value produces the interpolated value $\mu^*\xi_m = 183.1 \times 10^{-5}$. The binary interaction coefficients of this ternary system, A_{ij} and B_{ij}, are then calculated by using

TABLE 3. SUMMARY OF INTERACTION COEFFICIENTS A_{ij} AND B_{ij} OBTAINED FROM THE BINARY SYSTEMS OF THIS STUDY

System i — j	$\xi_i - \xi_j$	Obtained from experimental data A_{ij}	B_{ij}	Calculated values A_{ij}	B_{ij}
He—Ne	0.3344	−3.33	2.89	−3.11	2.99
He—A	0.3534	−2.93	2.75	−2.86	2.83
He—Kr	0.3626	−2.86	2.75	−2.73	2.76
H_2—Ne	0.1834	−6.78	5.93	−6.12	5.45
H_2—CH_4	0.1836	−6.50	5.52	−6.12	5.45
H_2—C_3H_8	0.1966	−5.88	5.49	−5.46	5.09
H_2—O_2	0.1999	−5.63	5.00	−5.40	5.00
H_2—A	0.2024	−5.40	4.86	−5.33	4.94
H_2—CO_2	0.2076	−5.22	4.85	−5.20	4.82
Ne—A	0.0190	−78.8	49.8	−95.1	52.6
Ne—Kr	0.0282	−53.2	41.0	−58.3	35.5
N_2—CO	0.0017	−1,220	740	−1,620	588
CO—C_2H_4	0.0046	−250	210	−500	217
N_2—C_2H_4	0.0051	−260	200	−438	196
C_2H_4—O_2	0.0055	−260	180	−401	182
A—Kr	0.0092	−285	120	−218	109
CO—O_2	0.0101	−300	90	−195	99
N_2—O_2	0.0106	−490	135	−186	94
C_3H_8—CO_2	0.0110	−280	90	−179	91
CH_4—C_3H_8	0.0130	−260	70	−146	77

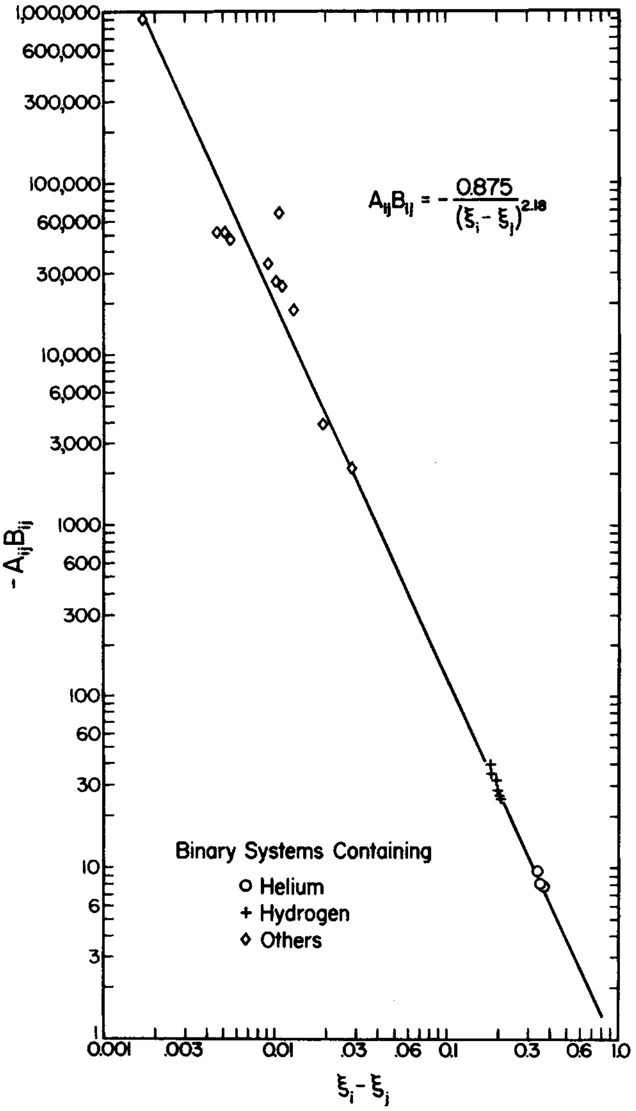
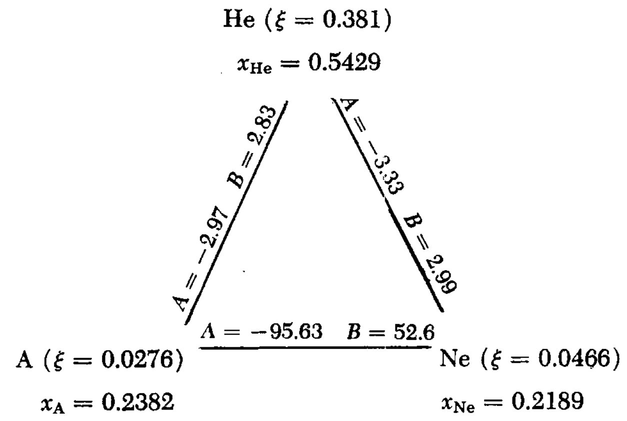


Fig. 6. Dependence of the product A_{ij} B_{ij} vs. ξ_i-ξ_j for the systems included in this study.

Equations (6), (7), and (9) to be as follows:

	$\xi_i - \xi_j$	A_{ij}	B_{ij}
Helium-neon	0.3344	− 3.33	2.99
Helium-argon	0.3534	− 2.97	2.83
Neon-argon	0.0190	−95.63	52.6

For this ternary system, the interlocking binary system dependences can be represented as follows:



These interaction coefficients, along with the respective mole fractions, produce the following viscosity parameter for the ternary mixture:

$$\xi_m = 0.2236 + \frac{(0.5429)(0.2189)}{-3.33 + 2.99(0.5429)}$$

$$+ \frac{(0.2189)(0.2382)}{-95.63 + 52.6(0.2189)} + \frac{(0.5429)(0.2382)}{-2.97 + 2.83(0.5429)}$$

$$= 0.2236 - 0.0695 - 0.0006 - 0.0904 = 0.0631$$

Therefore, $\mu^* = (183.1 \times 10^{-5})/0.0631 = 2{,}902 \times 10^{-5}$ centipoises. Saxena and Narayanan (7) report from this mixture an experimental value of $\mu^* = 2{,}957 \times 10^{-5}$ centipoises. From this approach, viscosities were calcu-

Table 4. Comparison Between Experimental Viscosity Measurements and Calculated Values for the Helium-Neon-Argon System at Atmospheric Pressure and 100°C.

Mole fraction							Viscosity, centipoise		Avg.
x_{He}	x_{Ne}	x_A	T'_c, °K.	T_R'	$\mu^* \xi_m$	ξ_m	exptl.	calc'd.	dev., %
0.1754	0.5576	0.2670	66.1	5.64	138×10^{-5}	0.0443	$3{,}237 \times 10^{-5}$	$3{,}115 \times 10^{-5}$	3.8
0.3594	0.3193	0.3213	64.7	5.77	145.8	0.0492	3,044	2,963	2.7
0.1983	0.2166	0.5851	99.1	3.76	105.8	0.0364	2,886	2,907	0.7
0.5429	0.2189	0.2382	48.5	7.69	183.1	0.0631	2,957	2,902	1.9

lated for three other mixtures of this ternary system for which experimental values exist (*7*). A comparison between experimental and calculated values for the four mixtures of this system is presented in Table 4. In general, the summation quantity of Equation (10) will be expanded into $k(k - 1)/2$ terms. Thus, for a ternary mixture, three terms are required, and, for a quaternary system, six terms will be needed.

RESULTS AND THEIR COMPARISON WITH METHOD OF WILKE

Viscosity parameters for mixtures ξ_m of the binary systems included in this study were calculated by using Equation (5) and the binary interaction coefficients B_{ij} with Equation (6) and A_{ij} with Equations (7), (8), and (9), respectively. These calculated interaction coefficients are presented in Table 3 for the systems included in this study.

Pseudocritical temperatures corresponding to the different binary mixtures permitted the calculation of values of $T_R' = T/T_c'$ and were used to obtain from Figure 1 the product $\mu^*\xi_m$ for each mixture. These products and the calculated viscosity parameter ξ_m produced for each mixture calculated viscosities which, when compared with corresponding experimental values, resulted in an average deviation of 1.86% for twenty-one points representing the three helium binary systems, 2.70% for forty-two points representing the six hydrogen binary systems, and 1.64% for eighty-five points representing the eleven other binary systems. The overall average deviation for a total of 148 points representing the twenty binary systems of this study is 1.97%.

Viscosities were also calculated for mixtures of the systems helium-nitrogen, hydrogen-nitrogen, argon-xenon, and krypton-xenon. These binary systems were not included in the development of Equations (5), (6), (7), (8), and (9). A comparison between calculated and experimental values produced for these systems the following deviations:

	Points	Avg. dev., %
Helium-nitrogen (*4*)	8	4.0
Hydrogen-nitrogen (*16*)	7	1.0
Argon-xenon (*10*)	11	0.6
Krypton-xenon (*10*)	11	2.3

The method of Wilke (*17*) was applied for the calculation of viscosities of mixtures for the twenty binary systems used for the development of this study. For 106 values, the average deviation between experimental measurements and values calculated by the method of Wilke was found to be 1.69%. Apparently, both methods produce viscosity values which give rise to average deviations of essentially the same order of magnitude.

In order to apply the method of Wilke, the viscosity and molecular weight of the pure components must be available. On the other hand, the present study requires that the viscosity parameter ξ_i be available for each pure component in order to establish the interaction coefficients A_{ij} and B_{ij}. This approach utilizes Equation (6) and Equations (7), (8), or (9) for the calculation of the viscosity interaction model represented by Equation (5) in conjunction with the use of the relationships of Figure 1.

ACKNOWLEDGMENT

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NOTATION

A_{ij}, B_{ij} = interaction coefficients, Equation (5)
k = number of components in mixture
M = molecular weight
R = gas constant
P_c = critical pressure, atm.
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_c' = pseudocritical temperature, °K.
T_R = reduced temperature, T/T_c
T_R' = pseudoreduced temperature, T/T_c'
v_c = critical volume, cc./g.-mole
x = composition, mole fraction
z_c = critical compressibility factor, $P_c v_c/RT_c$
μ^* = viscosity of gas at normal pressures, centipoise
ξ = viscosity parameter for pure substance, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
ξ' = pseudoviscosity parameter, Equation (11)
ξ_m = viscosity parameter for mixture, Equation (5)

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