The Prediction of the Viscosity of Nonpolar Binary Gaseous Mixtures at Atmospheric Pressure

MAILAND R. STRUNK, WAYNE G. CUSTEAD, and GERALD L. STEVENSON

University of Missouri, Rolla, Missouri

The transport properties of a gas depend on the forces between the molecules in a way that was first shown by Chapman and Enskog (*1*). Hirschfelder, Bird, and Spotz (*2, 3, 4*) have evaluated the collision integrals required in calculating the transport coefficients. They have also shown that the transport properties and the second virial coefficients for pure gases and gaseous mixtures may be calculated as a function of temperature. This information is also presented and discussed by Hirschfelder, Curtiss, and Bird (*5*). In this reference expressions are presented for computing the viscosities of multicomponent and binary gaseous mixtures from the appropriate pure component force parameters with the well-known combining laws to determine the force parameters of the mixture. With these expressions the agreement between the calculated and experimental values of binary viscosities for various nonpolar gaseous mixtures is quite good. These are summarized in references *3* and *4*. Rowlinson and Townley (*6*) have discussed the viscosities of pure and binary gaseous mixtures and have shown that the viscosities of several nonpolar gaseous mixtures agree within 1.5% with those calculated from the expressions presented by Hirschfelder, Curtiss, and Bird. Additional data on the viscosities of gases and mixtures are presented and discussed by Hilsenrath and Touloukian (*7*), Keyes (*8*), and Wilke (*9*).

While the expressions presented by Hirschfelder, Curtiss, and Bird for calculating binary and multicomponent gaseous viscosities are capable of showing good agreement, they are complicated and unwieldy expressions as far as ordinary engineering usefulness is concerned. In this work a very simplified approach to the calculation of viscosities for binary nonpolar gaseous mixtures is taken. This approach is based on a very simple model which assumes that the nonpolar gaseous molecules are rigid spheres and that the Lennard-Jones potential holds for all nonpolar mixtures and components over all temperature ranges. On the basis of these assumptions expressions are developed for determining the force parameters which are representative of the particular mixture and which require only a knowledge of the pure component Lennard-Jones force parameters and composition. Once these mixture parameters have been obtained, the binary viscosity calculation then becomes identical to that for a pure component gas. On the basis of 201 nonpolar binary mixtures covering a range of temperatures from 80° to 550°K. and atmospheric pressure the method predicts binary viscosities to within +5.5 and −6.7% of the actually observed viscosity 95% of the time. This loss in accuracy, when compared with the more rigorous expression of Hirschfelder, Curtiss, and Bird, is believed to be more than offset by the relative simplicity of the method presented.

METHOD OF CALCULATION

The procedure for calculating a binary nonpolar gaseous mixture utilizes the same form of an expression as that presented in reference 5 for determining a pure component viscosity. Only the combining laws are altered. The expression for determining the viscosity of a binary mixture is

$$\eta_{\text{mix}} = \frac{266.93 \times 10^{-7}\sqrt{T\,M_{\text{mix}}}}{\sigma^2_{\text{mix}}\,\Omega} \qquad (1)$$

The expressions for the Lennard-Jones force parameters for the mixture which are to be used in Equation (1) are

$$\sigma_{\text{mix}} = \sum_i X_i\,\sigma_i \qquad (2)$$

and

$$\frac{\epsilon_{\text{mix}}}{k} = \frac{\sum_i X_i\left[\frac{\epsilon_i}{k}\right]\sigma_i^3}{\left[\sum_i X_i\,\sigma_i\right]^3} \qquad (3)$$

DERIVATION OF THE COMBINING LAWS

For a binary mixture of gases (A) and (B), having mole fractions (X) and ($1 - X$), respectively, it is desired to have an expression

$$\Phi(r)_{\text{mix}} = 4\,\epsilon_{\text{mix}}\left[\left(\frac{\sigma_{\text{mix}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{mix}}}{r}\right)^{6}\right] \qquad (4)$$

where (ϵ_{mix}) and (σ_{mix}) are some combination of the pure component Lennard-Jones force parameters and the mole fraction of the components.

Owing to the rarity of three or more body collisions it is assumed that the collisions occurring in a mixture of (A) and (B) are only binary and represented by the molecular pairs (AA), (BB), (BA), and (AB). The characteristic diameter (σ) or collision diameter for these molecular pairs, with rigid spheres assumed, will be

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Wayne G. Custead is at Massachusetts Institute of Technology, Cambridge, Massachusetts. Gerald L. Stevenson is with the International Minerals and Chemical Corporation, Mulberry, Florida.

$$AA, \sigma_A = \frac{\sigma_A}{2} + \frac{\sigma_A}{2} = \sigma_A$$

$$BB, \sigma_B = \frac{\sigma_B}{2} + \frac{\sigma_B}{2} = \sigma_B$$

$$\left.\begin{matrix} AB \\ BA \end{matrix}\right\} \sigma_{AB} = \frac{\sigma_A}{2} + \frac{\sigma_B}{2} = \frac{\sigma_A + \sigma_B}{2}$$

Thus for a binary mixture the following statement can be written:

$$\sigma_{\text{mix}} = w_1 \sigma_A + w_2 \sigma_B + w_3 \left[\frac{\sigma_A + \sigma_B}{2} \right] \qquad (5)$$

where w_1, w_2 and w_3 are weighting factors dependent upon the relative number of molecular pairs (AA), (BB), and (AB), or (BA) present in the mixture. The problem of what is the expression for finding σ_{mix}, which is indicative of a particular mixture, becomes one involving probabilities. When one considers only those molecules involved in collisions at any given instant, the problem may be stated in another manner. Given (N) total balls, with (a) number of (A) and $(N - a)$ number of (B), what is the probability in withdrawing two balls at a time for the (AA), (BB), and (AB), or (BA) combinations? By carrying out a routine probability calculation in which $a = XN$, it can be shown that as $N \to \infty$, the probability for the various pairs are

$$P_{AA} = X^2$$
$$P_{BB} = (1 - X)^2$$
$$P_{AB} \text{ or } P_{BA} = 2X\,(1 - X)$$

also

$$\Sigma P = 1$$

Thus if (X) corresponds to mole fractions

$$\sigma_{\text{mix}} = X^2 \sigma_A + (1 - X)^2 \sigma_B + 2X\,(1 - X) \left[\frac{\sigma_A + \sigma_B}{2} \right] \qquad (6)$$

or

$$\sigma_{\text{mix}} = X \sigma_A + (1 - X)\, \sigma_B \qquad (7)$$

(σ_{mix}) is therefore weighted in accordance with the mole fraction in the mixture and is expressed in terms of the pure component parameters.

In order to find (ϵ_{mix}) a method somewhat analogous to that for obtaining (σ_{mix}) may be used. However a simple combination of the form

$$\epsilon_{\text{mix}} = w_1 \epsilon_A + w_2 \epsilon_B + w_3 \left[\frac{\epsilon_A + \epsilon_B}{2} \right]$$

cannot be used since (ϵ) a potential energy term is inherently different that (σ) a distance, and therefore one would not expect (ϵ) to be combined linearly in such a manner.

In determining the expression for (ϵ_{mix}) for the mixture the following assumptions have been made:

1. The individual molecules of a mixture of (A) and (B) are considered to be rigid spheres of radii $\sigma_A/2$ and $\sigma_B/2$, respectively (that is the closest distance of approach of like molecules would be σ_A or σ_B).
2. It is further assumed that the distance (R) between molecules is governed by the following statement:

$$P\,(r_1 < R < r_2 | r_1 > \sigma) = - \int_{r_1}^{r_2} K r^2 \,\Phi\,(r)\, dr$$

Since it is also assumed that $R \geqq \sigma$, (K) must be chosen so that

$$- \int_{\sigma}^{\infty} K r^2 \,\Phi\,(r)\, dr = 1$$

Physically this is equivalent to assuming that the probability of finding one molecule in a unit volume at a distance (r) from another molecule is directly proportional to the Lennard-Jones potential. The minus sign accounts for the fact that in the integration from $r = \sigma$ to $r = \infty$, $\Phi(r)$ is always negative. Thus for molecular pairs of the same species (i)

$$- \int_{\sigma}^{\infty} K r^2 \,\Phi\,(r)_i\, dr = 1$$

Substituting the Lennard-Jones expression for the ith species, that is

$$\Phi(r)_i = 4\,\epsilon_i \left[\left(\frac{\sigma_i}{r} \right)^{12} - \left(\frac{\sigma_i}{r} \right)^{6} \right]$$

into the probability expression and integrating, one gets

$$- \int_{\sigma}^{\infty} K r^2 \,\Phi\,(r)_i\, dr = C_i\, \epsilon_i\, \sigma_i^3 = 1$$

In a mixture of (A) and (B) molecules, since it is assumed that collisions of (AA), (BB), and (AB), or (BA) take place, the probability of finding an (A) most closely associated with another (A) molecule is not one but (X^2) as determined previously and shown in Equation (6). Thus for the mixture

$$C_{\text{mix}}\, \epsilon_{\text{mix}}\, \sigma_{\text{mix}}^3 = 1 = X^2 C_A\, \epsilon_A\, \sigma_A^3 + (1 - X)^2\, C_B\, \epsilon_B\, \sigma_B^3 + 2X\,(1 - X)\, C_{AB}\, \epsilon_{AB}\, \sigma_{AB}^3 \qquad (8)$$

The problem of determining an expression for $C_{AB}\, \epsilon_{AB}\, \sigma_{AB}^3$ in Equation (8) in terms of the pure component parameters still remains. This can be resolved by considering the force of attraction F_{AA} between two (A) molecules which is

$$F_{AA} = \frac{-\,d\Phi\,(r)_A}{dr}$$

The relative contribution of each molecule to this force, since they are identical molecules, is

$$F_A = \frac{1}{2} F_{AA} = \frac{1}{2} \left[- \frac{d\Phi\,(r)_A}{dr} \right]$$

Similarly for (B) molecules

$$F_B = \frac{1}{2} F_{BB} = \frac{1}{2} \left[- \frac{d\Phi\,(r)_B}{dr} \right]$$

When one assumes that these forces are characteristic of the individual molecules and not dependent in any way on the partner in a pair, then when an (A) and (B) are considered

$$F_{AB} = F_A + F_B = \frac{1}{2} \left[- \frac{d\Phi\,(r)_A}{dr} \right] + \frac{1}{2} \left[\frac{-\,d\phi(r)_B}{dr} \right] = - \frac{d\Phi\,(r)_{AB}}{dr}$$

and hence

$$\Phi\,(r)_{AB} = \frac{1}{2}\, [\Phi\,(r)_A + \Phi\,(r)_B]$$

or

$$\int_{\sigma}^{\infty} - K r^2 \,\Phi\,(r)_{AB}\, dr = \int_{\sigma}^{\infty} - K r^2 \left[\frac{\Phi(r)_A + \Phi(r)_B}{2} \right] dr = \frac{C_A\, \epsilon_A\, \sigma_A^3 + C_B\, \epsilon_B\, \sigma_B^3}{2}$$

Since the following is also true

$$- \int_{\sigma}^{\infty} K r^2 \,\Phi\,(r)_{AB}\, dr = C_{AB}\, \epsilon_{AB}\, \sigma_{AB}^3$$

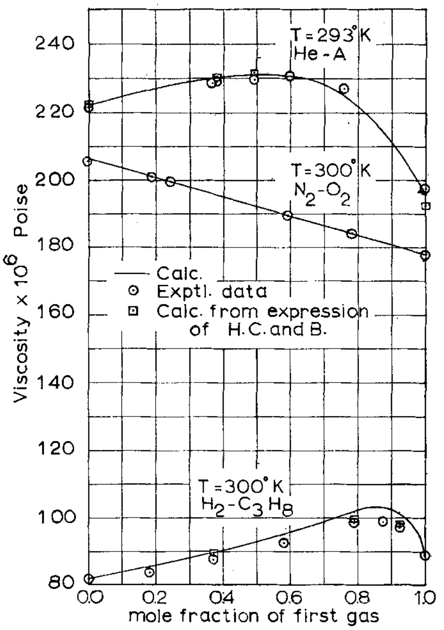

Fig. 1. A comparison of calculated viscosities of nonpolar binary mixtures with experimental data at various compositions for three typical systems.

It follows that

$$C_{AB}\,\epsilon_{AB}\,\sigma_{AB}{}^3 = \frac{C_A\,\epsilon_A\,\sigma_A{}^3 + C_B\,\epsilon_B\,\sigma_B{}^3}{2} \tag{9}$$

Substituting this result into Equation (8) and simplifying one obtains

$$\epsilon_{\text{mix}}\,\sigma_{\text{mix}}{}^3 = \frac{X\,C_A\,\epsilon_A\,\sigma_A{}^3}{C_{\text{mix}}} + \frac{(1-X)\,C_B\,\epsilon_B\,\sigma_B{}^3}{C_{\text{mix}}} \tag{10}$$

The nature of the constants C_A, C_B, and C_{mix} are such that

$$C_A\,\epsilon_A\,\sigma_A{}^3 = C_B\,\epsilon_B\,\sigma_B{}^3 = 1$$

and that

$$\frac{C_A\,\epsilon_A\,\sigma_A{}^3}{C_{\text{mix}}} = \frac{C_B\,\epsilon_B\,\sigma_B{}^3}{C_{\text{mix}}} = \epsilon_{\text{mix}}\,\sigma_{\text{mix}}{}^3$$

Equation (10 represents the final expression for $\epsilon_{\text{mix}}\,\sigma_{\text{mix}}{}^3$.

As a first approximation Equation (10) can be expressed as

$$\epsilon_{\text{mix}}\,\sigma_{\text{mix}}{}^3 = X\,\epsilon_A\,\sigma_A{}^3 + (1-X)\,\epsilon_B\,\sigma_B{}^3 \tag{11}$$

and

$$\epsilon_{\text{mix}} = \frac{X\,\epsilon_A\,\sigma_A{}^3 + (1-X)\,\epsilon_B\,\sigma_B{}^3}{(X\,\sigma_A + (1-X)\,\sigma_B)^3} \tag{12}$$

or finally

$$\frac{\epsilon_{\text{mix}}}{k} = \frac{X\left[\frac{\epsilon_A}{k}\right]\sigma_A{}^3 + (1-X)\left[\frac{\epsilon_B}{k}\right]\sigma_B{}^3}{(X\,\sigma_A + (1-X)\,\sigma_B)^3} \tag{13}$$

Equations (7) and (13) are expressed in general form by Equations (2) and (3). It is noted that the term $\left[\frac{\epsilon\,\sigma^3}{k}\right]$, derived from the authors' mathematical model, is identical to that found by Flynn and Thodos (*10*) by dimensional analysis considerations in their work on correlating pure component Lennard-Jones force constants with critical properties.

DISCUSSION

Among the 201 binary mixtures examined in this work thirty-six binary viscosities were experimentally determined by Stevenson (*11*) at three temperature levels over a range of about 100°C. These mixtures were composed of carbon dioxide, argon, air, and helium in varying amounts. A rolling ball viscometer, as described by Hubbard and Brown (*12*) and also in reference *11*, was used to obtain these particular viscosities. All analyses were obtained with a mass spectrometer. The remaining data examined in this work are from Landolt-Börnstein. A comparison of viscosity data given in these tables with that calculated from the expression of Hirschfelder, Curtiss, and Bird is conveniently summarized in references *3* and *4*. All calculations involving predicted viscosities were performed on an IBM-1620 digital computer.

Figure 1 presents three typical nonpolar binary gaseous mixtures which illustrate the effect of composition on viscosity. The solid lines represent the predicted viscosities as calculated by expressions (1), (2), and (3). The experimental viscosity data as well as that calculated from the more rigorous expression of Hirschfelder, Curtiss, and Bird were taken directly from reference *3* and superimposed on Figure 1. The prediction method presented in this work compares favorably with the experimental data and that calculated by the expression of Hirschfelder, Curtiss, and Bird for helium-argon and nitrogen-oxygen. The maximum deviation between the predicted and actual viscosity for the helium-argon and nitrogen-oxygen systems are −0.88% at 75.65% helium and −0.22% at 78.22% nitrogen. For the hydrogen-propane system the method predicts somewhat high. The maximum deviation between the predicted and the experimental viscosity is +4.95% and occurs at 92.25% hydrogen. However this is still within the limits of +5.5 and −6.7% within which all predictions would be expected to fall 95% of the time.

The 201 mixtures examined included eleven different gases at several temperature levels and in varying combinations. These included air, argon, carbon dioxide, ethane, helium, hydrogen, methane, neon, nitrogen, oxygen, and propane. Mixtures of helium and neon appeared to give consistently greater deviations along with mixtures of hydrogen and neon, especially at 550°K., although no general conclusions could be reached.

ACKNOWLEDGMENT

The authors wish to express their gratitude to the Mobil Oil Company, East St. Louis, Illinois, and the Monsanto Chemical Company, St. Louis, Missouri, for their helpfulness and cooperation in analyzing several of the binary gas samples used in this work. The helpful suggestions of Dr. C. E. Antle of the Mathematics Department are also gratefully acknowledged.

NOTATION

a = number of A molecules in a mixture
C = constant
F = force of attraction between molecules
K = constant for a given species of molecules, a normalizing factor
k = Boltzmann's constant, erg./molecule °K.
M = molecular weight
N = total number of molecules in a mixture
P = probability value
R = distance between two given molecules (that is the random variable)
r = distance between molecules
T = temperature, °K.
w = weighting factor
X = mole fraction

Greek Letters

ϵ = maximum energy of attraction of two molecules (a Lennard-Jones force parameter)

η = viscosity in poises
σ = zero energy collision diameter in (Å) (a Lennard-Jones force parameter)
$\Phi(r)$ = intermolecular potential energy function
Ω = appropriate value of the collision integral (a function of kT/ϵ)

Subscripts

A, B, AB = molecular pairs (AA), (BB), and (AB), or (BA), respectively
i = ith component or species
mix = gaseous mixture
1, 2, 3 = numbers associated with the molecular pairs (AA), (BB), and (AB), or (BA), respectively

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Manuscript received July 10, 1963; revision received January 15, 1964; paper accepted January 16, 1964. Paper presented at A.I.Ch.E. Memphis meeting.

Compressibility of Ammonia and its Mixtures with Nitrogen and Hydrogen

I. M. LICHTBLAU, R. H. BRETTON, and B. F. DODGE
Yale University, New Haven, Connecticut

OBJECTIVES AND SCOPE

The original objective of this work was to obtain compressibility data on the ternary system hydrogen-nitrogen-ammonia in order to permit calculations to be made of the effect of pressure on the equilibrium of the ammonia-synthesis reaction. For reasons which will be discussed presently the original objective was abandoned and the new one became the determination of the compressibility of pure ammonia and its mixtures with nitrogen at elevated pressures and temperatures.

An apparatus has been developed to take compressibility data from 500 to 2,500 atm. at temperatures ranging from 300° to 500°C. Compressibility data are presented for pure ammonia and a mixture of 19 mole % nitrogen and 81% ammonia at 350°, 400°, and 450°C. over the pressure range of 500 to 2,500 atm. Also data for pure ammonia at 300°C. and 500 to 1,500 atm. and a few points for the 37% nitrogen mixture at 350°C. are given.

REVIEW OF PREVIOUS WORK

Although a great many investigators have conducted compressibility studies on nitrogen and ammonia, very little work has been done above 300°C. and 1,000 atm. This review is confined to work either at 300°C. and above or at pressures greater than 1,000 atm. While Michels and co-workers (*23, 24*) provide the most accurate data on nitrogen to a pressure of 6,000 atm., the temperature range extends only to 150°C. Bartlett and co-workers (*1, 2*) conducted experiments to 400°C. but limited the pressures to 1,000 atm. Benedict (*4*) conducted a very thorough study of nitrogen at 5,800 atm., but the top temperature was 200°C. Recently Saurel and co-workers (*27*) have extended the ranges of temperature and pressure for this gas to 1,000°C. and 1,000 atm.

Ammonia has not been studied as extensively as nitrogen. Meyers and Jessup (*20*) did some early work to 300°C. and 28 atm. Beattie and Lawrence (*3*) obtained data at temperatures as high as 325°C. but limited the pressure to 130 atm.

More recent work was done by two investigators in Russia. Kazarnovskii (*15, 16*) has done considerable work on the ammonia, nitrogen, hydrogen system, and he also studied pure ammonia from 150° to 300°C. and 100 to 1,600 atm. This present study presents data that can be compared with the work of Kazarnovskii on ammonia at 300°C. and from 500 to 1,600 atm. Tsiklis (*28*) investigated ammonia compressibility at 150°C. and pressures in the range of 1,000 to 10,000 atm.

In contrast to the considerable amount of work that has been performed on the pure gases relatively little has been accomplished with mixtures of the two. Only one

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I. M. Lichtblau is with the California Research Corporation, Richmond, California.