The Prediction of the Viscosity of Multicomponent, Nonpolar Gaseous Mixtures at Atmospheric Pressure

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The method for predicting the viscosity of binary nonpolar gaseous mixtures from pure component Lennard-Jones force parameters and composition has been extended to multicomponent mixtures. The 136 mixtures examined contained from three to seven components from sixteen different gases in the temperature range from 5° to 1,014°C. The predicted gaseous viscosities should fall between —0.3 and —6.7% of the actual viscosities 95% of the time. With a slight modification of the constant in the viscosity expression, the viscosity can be predicted to within ±3.2% of the experimental viscosity 95% of the time for mixtures containing three or more components.

Several methods, both rigorous and empirical, have been developed for predicting the viscosities of multicomponent gaseous mixtures. Unfortunately, most of these methods are either unwieldly, require prolonged calculations, or necessitate a knowledge of the pure component viscosity at given temperatures. Such data are often not available.

In a previous work, Strunk, Custead, and Stevenson (1) presented a method for predicting the viscosities of binary, nonpolar gaseous mixtures. The purpose of the present paper is to show that the prediction methods for binary, nonpolar gases can be applied to the prediction of the viscosity of multicomponent, nonpolar gases containing as many as seven components. In this work the same simplified approach is used as for the binary, nonpolar mixtures. This approach is based on a simplified 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, the combining expressions proposed in reference 1 are applied to nonpolar multicomponent mixtures for determining the force parameters which are considered to be representative of the particular mixture. These expressions require only a knowledge of the pure component Lennard-Jones force parameters and composition. Once these mixture parameters have been obtained, the multicomponent viscosity calculation becomes identical to that for a pure component gas.

PRESENT METHODS OF CALCULATION

There are several methods in existence for predicting or calculating gaseous viscosities. In 1926 Trautz (2, 3) developed expressions for calculating the viscosity for both binary and ternary gaseous mixtures. In order to use this method, values of the pure component viscosity were required at the desired temperature as well as values of the molecular diameter.

Herning and Zipperer (4) in 1936 also proposed an expression for calculating the viscosity of a mixture of gaseous components. Their expression affords a simple means for calculating the viscosity of gaseous mixtures provided the values of the viscosities are known for each pure component at the particular temperature desired.

In 1949, Curtiss and Hirschfelder (5, 6), presented expressions for predicting the gaseous viscosity of an n-component mixture. Their expressions were obtained from the rigorous kinetic theory of multicomponent gas mixtures. The method, although tedious and lengthy, requires only a knowledge of the pure component Lennard-Jones force constants and composition. Their method predicts viscosity values that are in very good agreement with experimental values (7, 8, 9).

Also, in 1949, Buddenberg and Wilke (10) developed a semiempirical equation for mixture viscosities based on the earlier work of Sutherland (11), Thiesen (12), and Schudel (13). The diffusion coefficient is used in their equation to take into account the collisions between unlike pairs of molecules. The application of their equations is contingent upon a knowledge of the pure component viscosities, densities, and Lennard-Jones force parameters. In 1950, Wilke (14) extended this work and presented expressions for predicting multicomponent gaseous viscosities based on a knowledge of the pure component viscosity at the desired temperature.

A semiempirical expression was published in 1962 by Saxena and Gambhir (15) and was produced from the work of Wright and Gray (16). Their empirical formula also required values of the pure component viscosity as well as related binary viscosities at any composition.

PROPOSED PREDICTION METHOD

In reference 1 a method was presented for combining the individual pure component Lennard-Jones force parameters into one set of parameters that were assumed to be representative of the particular mixture. From these, a value for the appropriate reduced collision integral could be obtained. Once the parameters and the collision integral value have been obtained, the calculation for the viscosity of a multicomponent mixture is no

more involved than that for a pure component gas. Only the pure component Lennard-Jones force parameters and composition are required. This expression is

$$\eta_{mix} = \frac{266.93 \times 10^{-7}\sqrt{TM_{mix}}}{\sigma_{mix}^2 \, \Omega_{mix}^{(2,2)*}} \quad (1)$$

where

$$\sigma_{mix} = \sum_{i=1}^{n} X_i \sigma_i \quad (2)$$

$$M_{mix} = \sum_{i=1}^{n} X_i M_i \quad (3)$$

$$\frac{\epsilon_{mix}}{k} = \frac{\sum_{i=1}^{n} X_i \left(\frac{\epsilon_i}{k}\right) \sigma_i^3}{\sigma_{mix}^3} \quad (4)$$

The viscosities of fourteen ternary and ten quaternary gaseous mixtures containing air, argon, carbon dioxide, methane, and helium were experimentally determined by Fehsenfeld (17) at 5°, 50°, and 90°C. and 760 mm. Hg. These seventy-two measured viscosities are compared with the calculated viscosities of Equation (1) and tabulated in reference 17. All calculations in this work were performed with an IBM-1620 computer.

A comparison of the predicted viscosities was made with the experimental viscosities of eight ternary mixtures of helium, neon, and argon at 20°, 100°, and 200°C. and 760 mm. Hg. published by Trautz in reference 3. These published viscosities have also been tabulated by Fehsenfeld. Also tabulated in reference 17 and compared with the predicted viscosities of Equation (1) are the data presented in reference 7 by Hirschfelder, Curtiss, and Bird, and those of Carr (18). Thirty-seven mixtures, composed of three to seven components, containing various proportions of carbon dioxide, oxygen, carbon monoxide, hydrogen, nitrogen, methane, and heavier hydrocarbons between the temperatures of 20° and 1,014°C. were examined from reference 7. Two different hydrocarbon mixtures containing five and seven components were published by Carr (18) and provided an additional four experimental values for comparison purposes.*

Based on a statistical treatment of 136 multicomponent viscosities, the predicted viscosity from Equation (1) can be expected to fall between -0.3 and -6.7% of the experimental viscosity 95% of the time. All predicted viscosities fell slightly under the observed values. Equation (1), when applied to binary, nonpolar gaseous mixtures, gave 95% confidence limits of +5.5 to -6.7%. In order to eliminate the negative trend in the predicted viscosities for multicomponent mixtures, it is suggested that the constant in Equation (1) be slightly adjusted. Such a modification would take into account the complex interactions between the molecules in a multicomponent mixture which are not adequately described by the Lennard-Jones potential. Similar recommendations have been suggested in the past by other investigators (19).

On the basis of this work and that described in reference 1, it is recommended that Equation (1) be used for predicting the viscosity of binary, nonpolar gaseous mixtures. For predicting the viscosities of nonpolar gaseous mixtures containing three or more components, the following expression is recommended:

$$\eta_{mix} = \frac{276.27 \times 10^{-7}\sqrt{TM_{mix}}}{\sigma_{mix}^2 \, \Omega_{mix}^{(2,2)*}} \quad (5)$$

Equations (2), (3), and (4) are still applicable. With Equation (5) the predicted viscosity for nonpolar gaseous mixtures containing three or more components should fall between +3.2 and -3.2% of the actual viscosity 95% of the time.

NOTATION

k = Boltzmann's constant, erg./molecule °K.
M = molecular weight, g./g.-mole
T = absolute temperature, °K.
T^* = reduced temperature, kT/ϵ, dimensionless
X = mole fraction

Greek Letters

ϵ = maximum energy of attraction between two molecules, Lennard-Jones parameter, erg./molecule
ϵ/k = ratio of ϵ to Boltzmann's constant, °K.
η_{mix} = predicted coefficient of viscosity for a mixture, g./cm. sec.
σ = characteristic collision diameter, Lennard-Jones parameter, °A.
$\Omega^{(2,2)*}$ = reduced collision integral for viscosity, function of the reduced temperature (T^*), dimensionless

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