Calculation of Viscosity and Diffusion Coefficients of Nonpolar Gas Mixtures at Ordinary Pressures

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The knowledge of momentum and mass transfer in gas phase is very important for a large number of pure and applied problems. The kinetic theory for nonpolar gases and their multicomponent mixtures at ordinary pressures is sufficiently developed (*1, 2*) so that the coefficients of viscosity and diffusion can be calculated. These values are quite reliable for spherically symmetric molecules but become less so with the complexity of the molecules. The calculations are cumbersome because tedious computation is not only involved, but also it is essential to know the intermolecular potential for which the necessary collision integrals are already evaluated. Since the increase in the number of components in the mixture increases the computational task, attempts have been made to simplify this procedure as well as the formula. Many semitheoretical and empirical procedures have been developed. Here we describe a new method which can correlate the viscosity data for binary systems, provided one such mixture value be known at any composition as those of the related pure components. The method can then predict binary diffusion and multicomponent viscosities at that temperature, as well as at higher temperatures, provided the data on viscosity of related pure gases are available.

THE PROPOSED PROCEDURE FOR CALCULATION OF VISCOSITY

The rigorous theoretical expression of viscosity for a multicomponent mixture can be reduced to the following form (*3*):

$$\eta_{\text{mix}} = \sum_{i=1}^{n} \frac{\eta_i}{1 + \sum\limits_{\substack{j=1 \\ j=i}}^{n} \Phi_{ij} \dfrac{x_j}{x_i}} \tag{1}$$

where

$$\Phi_{ij} = \frac{6}{5} A_{ij}{}^{*} \frac{RT}{PM_i} \frac{\eta_i}{D_{ij}} \tag{2}$$

The form of Equation (1) is approximate (*4*) as is the expression for Φ_{ij} (*5*). However, with some empirical adjustment both these relations have proved very successful in correlating the data on viscosities. We then employ Equation (2) to write

$$\frac{\Phi_{ij}}{\Phi_{ji}} = \frac{\eta_i M_j}{\eta_j M_i} \tag{3}$$

and determine Φ_{ij} and Φ_{ji} on the basis of Equation (3) and one experimental value of η_{mix} for the binary system. This procedure will now be tested by performing calculation for a large number of systems where experimental data are available.

We report here in brief only the final results of our detailed numerical experimentation, (*6*). We have examined twenty two binary systems. These are: Xe-Kr, Xe-Ar, Xe-Ne, Xe-He, Kr-Ar, Kr-Ne, Kr-He, Ar-Ne, Ar-He, Ne-He, Ar-H_2, Ne-H_2, He-H_2 O_2-H_2, N_2-NO, O_2-CO, N_2-CO_2, H_2-CO_2, H_2-CH_4, O_2-C_2H_4, N_2-C_2H_4 and CH_4-C_2H_6.

The data for the first seven systems, are available as a function of composition at 291°K., and could be successfully reproduced. The average absolute deviation for all the sixty-two mixtures is 0.9% and this improves to 0.7% if ten mixtures of He-Xe system are ignored. Calculations for the remaining fifteen systems are equally successful and the data are also available for several temperatures. The computed viscosity values agree with the experimental values within an average absolute deviation of 0.5%. The high temperature viscosity values could be correlated on the basis of Φ_{ij} evaluated at the lowest temperature within an average absolute deviation of 0.8%. This result is not very startling as in Equation (2) both $A_{ij}{}^{*}$ and $(\eta_i T/PD_{ij})$ and hence Φ_{ij} are only feebly dependent on temperature (*7*).

Viscosities were also computed for the ternary system Ar-Ne-He. For the twelve mixtures referring to three temperatures, the calculated results agree with the experimental values within an average absolute deviation of 0.4%. The results on eight mixtures at the two higher temperatures are reproduced within an average absolute deviation of 0.6% when Φ_{ij} values determined at the lowest temperature are used. Thus, the conclusions on binary and ternary systems are alike, and it is reasonable to believe that multicomponent viscosities can also be reproduced in the same way.

Similar methods are developed for the correlation and calculation of viscosity of multicomponent mixtures, by Buddenberg and Wilke (*8*), Wilke (*9*), Saxena and Gambhir (*10, 11*), and Gambhir and Saxena (*7, 12*). The method currently suggested is as competent as any of these.

THE PROPOSED PROCEDURE FOR CALCULATION OF DIFFUSION

It is interesting to examine the relation of Equation (2) for estimating diffusion coefficients. As the relation is approximate, a semiempirical adjustment is desirable. We have examined the experimental data for the systems He-Ne, He-Ar, He-Xe, Ne-Ar, Ar-Xe, H_2-He, H_2-Ar, H_2-O_2, H_2-CO_2, O_2-CO, N_2-NO, N_2-C_2H_4, O_2-C_2H_4 and CH_4-C_2H_6 and suggest the following relation for estimating diffusion coefficients:

$$D_{ij} = \frac{1.54\, RT\, \eta_i}{PM_i\Phi_{ij}} \tag{4}$$

The numerical constant was obtained by the least square fit on twenty-seven measurements of these fourteen systems. Equation (4) reproduces these directly measured values within an average absolute deviation of 7.2%. The tabulated results are given elsewhere (*6*).

Further, as Φ_{ij} are weakly dependent on temperature, it is not necessary to evaluate Φ_{ij} at the temperature of interest for use in Equation (4). This immediately suggests that D_{ij} at higher temperatures can be easily evaluated from relation (*4*), provided we know the values of viscosities for either of the pure components at those very temperatures and Φ_{ij} at any temperature. This is a very promising and useful result. The accuracy of such a procedure is tested by detailed numerical calculations where directly observed values are available. For the fifteen systems namely, He-Kr, Ne-Kr, Ar-Kr, Ne-Xe, Ne-Ar, He-Xe, Ar-Xe, He-Ar, He-Ne, H_2-Ne, H_2-Ar, H_2-O_2, O_2-CO, H_2-CO_2, and N_2-CO_2 and their 139 measurements, Equation (4) reproduces the observed values within an average absolute deviation of 8.4%. The details of these calculations and references to the experimental diffusion values and related data are given in (*6*).

It is not intended here to make a detailed comparison of the different methods and their relative merits and demerits which are used for calculating the diffusion coefficient. We simply mention the different methods and list in Table 1 some of the statistical deviations quoted by three workers. This will provide some idea of the success and relative footing of the proposed method. The methods very often used for the calculation of diffusion coefficients are: Gilliland (*13*), Andrussow (*14*), Arnold (*15*), Chen and Othmer (*16*), Slattery and Bird (*17*), Othmer and Chen (*18*), Fuller, Schettler and Giddings (*19*), and Saksena and Saxena (*20*).

TABLE 1. SUMMARY OF RESULTS: ON THE CALCULATION OF DIFFUSION COEFFICIENT BY DIFFERENT METHODS

Method	% dev.[a]	% dev.[b]	% dev.[c]
Rigorous Theory (*1, 2*)	7.2	6.4	—
Gilliland (*13*)	20.1	21.1	39.3
Andrussow (*14*)	15.0	16.4	—
Arnold (*15*)	8.5	10.7	6.9
Chen and Othmer (*16*)	8.1	8.9	—
Slattery and Bird (*17*)	14.1	14.0	6.0
Othmer and Chen (*18*)	16.6	13.9	—
Fuller, Schettler and Giddings (*19*)	4.2	4.3	—
Saksena and Saxena (*20*)	—	—	4.3

a. Due to Fuller and Giddings (*21*) and refer to 38 systems and 47 different experimental points.

b. Due to Fuller, Schettler and Giddings (*19*) and refer to 340 diffusion measurements.

c. Due to Saksena and Saxena (20) and refer to 52 experimental values of 5 systems.

A critical look of Table 1 establishes the adequacy of the proposed method. Some of its other special attractive features are the simplicity, relatively small initial input information, possible extension to high temperatures, and simultaneous correlation and generation of viscosity data.

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NOTATION

A_{ij}^* = ratio of the reduced collision integrals, subscripts indicate the two molecular species *i* and *j* in the mixture
D_{ij} = diffusion coefficient for the gases *i* and *j*
M = mol. wt.
n = number of components in a multicomponent mixture
P = pressure of the gas or gas mixture
R = gas constant
T = temperature in °K.
X_i = mole fraction of the *i*th component in the mixture
η_i = viscosity of the *i*th gas
η_{mix} = viscosity of the mixture
Φ_{ij} = constant of the Sutherland equation referring to the mixture of gases *i* and *j*.

LITERATURE CITED

1. Chapman, S., and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases", Cambridge University Press, London (1952).
2. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", John Wiley, New York (1964).
3. Brokaw, R. S., *J. Chem. Phys.*, **29**, 391 (1958).
4. Burnett, D., *ibid.*, **42**, 2533 (1965).
5. Brokaw, R. S., *ibid.*, **42**, 1140 (1965).
6. Material has been deposited as document #9883 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D.C., and may be obtained for $2.50 for photoprints or $1.75 for 35 mm. microfilm.
7. Gambhir, R. S., and S. C. Saxena, *Trans. Faraday Soc.*, **60**, 38 (1964).
8. Buddenberg, J. W., and C. R. Wilke, *Ind. Eng. Chem.*, **41**, 1345 (1949).
9. Wilke, C. R., *J. Chem. Phys.*, **18**, 517 (1950).
10. Saxena, S. C., and R. S. Gambhir, *Proc. Phys. Soc.*, **81**, 788 (1963).
11. ———, *Indian J. Pure Appl. Phys.*, **1**, 208 (1963).
12. Saksena, M. P., and S. C. Saxena, *Proc. Natl. Inst. Sci. India, P. A.* **31**, 18 (1965)
13. Gilliland, E. R., *Ind. Eng. Chem.*, **26**, 681 (1934).
14. Andrussow, L., *Z. Electrochem.*, **54**, 566 (1950).
15. Arnold, J. H., *Ind. Eng. Chem.*, **22**, 1091 (1930).
16. Chen, N. H., and D. F. Othmer, *J. Chem. Eng. Data*, **7**, 37 (1962).
17. Slattery, J. C., and R. B. Bird, *AIChE J.*, **4**, 137 (1958).
18. Othmer, D. F., and H. T. Chen, *Ind. Eng. Chem. Process Design Develop.*, **1**, 249 (1962).
19. Fuller, E. N., P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.*, **58**, 18 (1966).
20. Saksena, M. P., and S. C. Saxena, *Indian J. Pure Appl. Phys.*, **4**, 109 (1966).
21. Fuller, E. N., and J. C. Giddings, *J. Gas Chrom.*, **3**, 222 (1965).