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EFFECT OF HIGHER CHAPMAN-ENSKOG APPROXIMATIONS

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Determination of Diffusion Coefficients from Viscosity Measurements: Effect of Higher Chapman–Enskog Approximations

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Numerical calculations based on the higher Chapman–Enskog approximations show that mutual diffusion coefficients calculated from binary mixture viscosity data agree within experimental uncertainty with the measured D_{12} values at compositions corresponding to a trace of the heavy component.

I. INTRODUCTION

IN the first Chapman–Enskog approximation, the viscosity of a binary gas mixture, $[\eta_{\mathrm{mix}}]_1$, is related to the mutual diffusion coefficient of the gas pair, $[D_{12}]_1$, in a manner nearly independent of assumptions about the intermolecular forces. If experimental values of η_{mix} are used in this formula, values of D_{12} can be calculated for monatomic and homonuclear diatomic gases which are generally in good agreement with directly measured values.[1] Although the Chapman–Enskog theory strictly applies only to molecules without internal degrees of freedom, the form of the relationship between $[\eta_{\mathrm{mix}}]_1$ and $[D_{12}]_1$ remains unchanged when inelastic collisions are considered.[2] Weissman[3] has verified that D_{12} values estimated from experimental η_{mix} for polyatomic and polar gases also compare favorably with direct measurements.

The advantage of the determination of D_{12} from η_{mix} is that it provides a method for obtaining D_{12} values under conditions where direct diffusion measurements are difficult to make. Even though accuracy is lost in making the calculation, the viscosity data are usually accurate enough that the final calculated D_{12} involves no more experimental uncertainty than many directly measured values. In some cases, the viscosity derived D_{12} have in fact proved superior.[4,5]

There remains the problem that all of these calculations involve only the Chapman–Enskog first approximations. Thus $[D_{12}]_1$ is independent of mixture composition, whereas experimental values of D_{12} may vary several percent with composition. Burnett[6] has pointed out that the values of D_{12} calculated from η_{mix} cannot be true D_{12} values, since they are calculated from a theoretical first approximation; neither can they be correct $[D_{12}]_1$ values, since experimental values of η_{mix} are used in a formula for $[\eta_{\mathrm{mix}}]_1$.

The purpose of this paper is to clarify the status of D_{12} values calculated from η_{mix}, by investigation of higher Chapman–Enskog approximations. Numerical calculations with these higher approximations show that the calculated D_{12} values have a weak composition dependence, but are not true D_{12} values. They can, however, be taken equal to the experimental value of D_{12} at trace concentration of the heavy component of the mixture, without incurring any error as large as current experimental uncertainties.

II. EQUATIONS

The Chapman–Enskog equation for the mth approximation to the viscosity of a binary gas mixture is[7]

$$[\eta_{\mathrm{mix}}]_m = \frac{5(2\pi kT)^{\frac{1}{2}}}{4\pi\sigma_{12}{}^2}\left(\frac{m_1 m_2}{m_1 + m_2}\right)^{\frac{1}{2}}$$

$$\times\left(\frac{x_1{}^2\mathfrak{B}_{11}{}^{(m)} - 2x_1 x_2 \mathfrak{B}_{1-1}{}^{(m)} + x_2{}^2\mathfrak{B}_{-1-1}{}^{(m)}}{x_1 x_2 \mathfrak{B}^{(m)}}\right), \quad (1)$$

where k is Boltzmann's constant, σ_{12} is a characteristic distance parameter of the pair potential function, m_1 and m_2 are the molecular masses of the components, and x_1 and x_2 are their mole fractions. The determinant $\mathfrak{B}^{(m)}$ is symmetrical and of order $2m$ with elements b_{ij}, where i and j range from $-m$ to m, excluding zero. The determinant $\mathfrak{B}_{ij}{}^{(m)}$ is the minor of $\mathfrak{B}^{(m)}$ obtained by striking out the row and column containing b_{ij}. The b_{ij} can be expressed as linear combinations of the collision integrals $\Omega^{(l,s)*}$ by evaluation of a set of bracket integrals.[7] The b_{ij} elements for $m = 1$ have been given by Chapman and Cowling,[7] and those for $m = 2$ by Saxena and Joshi.[8] We have verified all of these expressions and used them in the present work. Seven types of collision integrals are required for the $m = 2$ computation: $l = 1$, $s = 1$, 2, 3; $l = 2$, $s = 2$, 3, 4; and $l = 3$, $s = 3$. Joshi[9] has also evaluated the additional b_{ij} needed for the $m = 3$ approximation, but these are

* On sabbatical leave, 1965–1966, from the Chemical Engineering Department, University of Missouri, Columbia, Mo.
[1] S. Weissman and E. A. Mason, J. Chem. Phys. **37**, 1289 (1962).
[2] L. Monchick, K. S. Yun, and E. A. Mason, J. Chem. Phys. **39**, 654 (1963).
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[6] D. Burnett, J. Chem. Phys. **42**, 2533 (1965).

[7] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1952), 2nd ed.
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[9] R. K. Joshi, Phys. Letters **15**, 32 (1965).

not needed in the present work because the $m=2$ approximation is accurate enough. Joshi was apparently misled by some calculations in Chapman and Cowling which indicate that the third approximation to η_{mix} for a Lorentzian gas mixture contributes about 2%. These calculations only apply to that part of the stress tensor due to the light component of the mixture, but in a real mixture of the Lorentzian type the major contribution to the stress tensor is made by the heavy component. In other words, the 2% contribution refers only to a small fraction of the true viscosity.

The Chapman–Enskog first and second approximations to D_{12} have been discussed in detail,[7,10] and there is no need to repeat the formulas here. The calculations for $[D_{12}]_2$ can be carried out with the same set of collision integrals required for $[\eta_{mix}]_2$.

For $m=1$, Eq. (1) gives an expression which is linear in η_{mix} and quadratic in D_{12}, with coefficients that are functions of the mole fractions, molecular masses, and viscosities of the two component gases.[1,3] The corresponding expression for $m=2$ is much more complicated.

III. CALCULATIONS

The numerical calculations are primarily concerned with mixtures of gases with rather dissimilar molecules. The theoretical formulas are expected to be accurate for mixtures of similar molecules, since they are known to be accurate in the limiting case of a mixture of a gas with itself,[7,10] which is the same as a single pure gas. Molecular weights and exp-6 potential parameters[11] have been used which correspond to the mixtures He–Ar, He–Kr, He–Xe, and Kr–Xe, although the
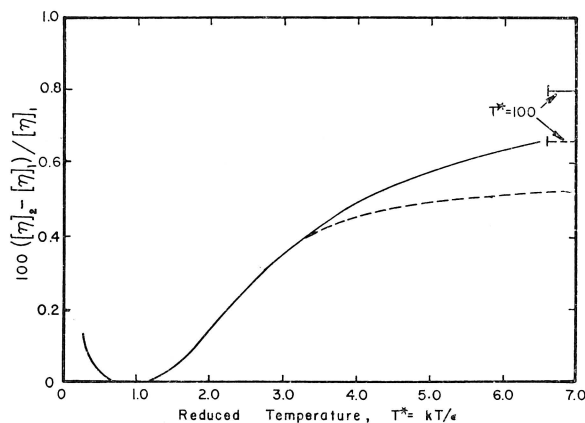

FIG. 1. Contribution of the higher Chapman–Enskog approximations to the viscosity of a pure gas: —— third approximation, 12–6 potential; ------ second approximation, exp-6 potential.

[10] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1964), 2nd ed. See also E. A. Mason, J. Chem. Phys. **27**, 75 (1957).

[11] E. A. Mason, J. Chem. Phys. **23**, 49 (1955).

TABLE I. The minimum and maximum contributions to η_{mix} from the second Chapman–Enskog approximations.

T (°K)	$100([\eta_{mix}]_2-[\eta_{mix}]_1)/[\eta_{mix}]_1$			
	He–Ar	He–Kr	He–Xe	Kr–Xe
70	0.00–0.54	0.01–0.54	0.08–0.54	0.01–0.12
100	0.01–0.56	0.01–0.56	0.02–0.56	0.01–0.20
200	0.06–0.57	0.01–0.57	0.01–0.57	0.00–0.01
500	0.45–0.65	0.28–0.60	0.13–0.60	0.13–0.28
1000	0.64–0.66	0.50–0.66	0.44–0.66	0.44–0.66

results can also be viewed as pure numerical experimentation without reference to any specific real system.

A. Viscosities

A brief summary of the calculations of $[\eta_{mix}]_1$ and $[\eta_{mix}]_2$ is given in Table I. In general it can be seen that the second approximations differ but little from the first approximations; the first approximation to η_{mix} is therefore presumably accurate. The second approximation makes the largest contribution when the mixture contains a trace of the heavy component. This is in marked contrast to the thermal conductivity of a binary mixture, both in over-all accuracy and in the composition range where the first approximation is least accurate, for the Chapman–Enskog formulas for the thermal conductivity can be rather inaccurate in the range where the light component is in low concentration.[12] The physical reason for this behavior is not hard to understand, given the knowledge that the Chapman–Enskog formulas give a rather inaccurate description of the collision of a few light, fast molecules with a collection of heavy, stationary molecules (Lorentzian mixture).[7] When a mixture has the light component in low concentration, the thermal conductivity is dominated by such collisions because the light molecules are still the main energy carriers. The viscosity, however, is dominated by the motion of the heavy molecules, and collisions with a few light molecules scarcely affect the trajectories of heavy molecules.

The behavior of $[\eta_{mix}]_2/[\eta_{mix}]_1$ as a function of composition and temperature does not need to be reported in detail, since it can be understood in terms of the corresponding behavior for a single gas. It is well known that the contribution of the higher approximations for a single gas depends on the reduced temperature as shown in Fig. 1.[10] The significant feature here is the minimum at about $T^*=1$. Whenever the reduced temperatures of the pure components are nearly equal, the contribution of the second approximation to η_{mix} is nearly independent of composition, since the mixture then behaves roughly as a mixture of a gas with itself. If the pure component reduced temperatures are different but both are greater than 1,

[12] E. A. Mason and S. C. Saxena, J. Chem. Phys. **31**, 511 (1959).

TABLE II. First and second Chapman–Enskog approximations to D_{12} compared with the apparent value calculated from η_{mix} using the formula for $[\eta_{mix}]_1$.

T (°K)	x_1[a]	He–Ar			He–Kr		
		$[D_{12}]_1$	$[D_{12}]_2$	$[D_{12}]_{app}$	$[D_{12}]_1$	$[D_{12}]_2$	$[D_{12}]_{app}$
70	0.01	0.05742	0.05776	0.05758	0.05185	0.05195	0.05190
	0.99	0.05742	0.05761	0.05748	0.05185	0.05192	0.05183
100	0.01	0.1103	0.1117	0.1101	0.08964	0.09155	0.08997
	0.99	0.1103	0.1111	0.1106	0.08964	0.09085	0.08972
200	0.01	0.3714	0.3800	0.3750	0.3522	0.3590	0.3556
	0.99	0.3714	0.3761	0.3732	0.3522	0.3571	0.3532
500	0.01	1.775	1.822	1.788	1.723	1.770	1.739
	0.99	1.775	1.800	1.784	1.723	1.756	1.729
1000	0.01	5.789	5.937	5.828	5.716	5.872	5.759
	0.99	5.789	5.868	5.820	5.716	5.825	5.733

T (°K)	x_1[a]	He–Xe			Kr–Xe		
		$[D_{12}]_1$	$[D_{12}]_2$	$[D_{12}]_{app}$	$[D_{12}]_1$	$[D_{12}]_2$	$[D_{12}]_{app}$
70	0.01	0.04157	0.04158	0.04156	0.004412	0.004412	0.004414
	0.99	0.04157	0.04158	0.04151	0.004412	0.004412	0.004414
100	0.01	0.08458	0.08493	0.08484	0.009069	0.009070	0.009069
	0.99	0.08458	0.08488	0.08466	0.009069	0.009070	0.009070
200	0.01	0.3004	0.3068	0.3033	0.03717	0.03717	0.03718
	0.99	0.3004	0.3056	0.3011	0.03717	0.03717	0.03718
500	0.01	1.472	1.512	1.491	0.2152	0.2160	0.2157
	0.99	1.472	1.504	1.476	0.2152	0.2158	0.2157
1000	0.01	4.835	4.966	4.887	0.7372	0.7431	0.7404
	0.99	4.835	4.941	4.850	0.7372	0.7422	0.7401

[a] Component 1 is the first of the pair as listed.

the contribution is monatonic with composition. If the pure component reduced temperatures straddle the minimum—e.g., $T_1^* > 1.0$ and $T_2^* < 0.75$—then the contribution shows a minimum with varying composition. These generalizations are consistent with the few numerical calculations reported by Saxena and Joshi.[8]

B. Diffusion Coefficients

Of most interest for the present purpose is the status of values of D_{12} calculated from the expression for $[\eta_{mix}]_1$ with experimental values used for the pure component viscosities. For this purpose we pretend that the calculated values of $[\eta_{mix}]_2$, $[\eta_1]_2$, and $[\eta_2]_2$ represent experimental values, and calculate apparent diffusion coefficients $[D_{12}]_{app}$ by substituting these values into the quadratic expression for $[\eta_{mix}]_1$. Some of the results are shown in Table II, only two extreme mixture compositions being listed. Shown for comparison are the values of $[D_{12}]_1$ and $[D_{12}]_2$ calculated by the Chapman–Enskog approximation.[7,10] The happiest situation would be for $[D_{12}]_{app}$ to be equal to $[D_{12}]_2$. Although $[D_{12}]_{app}$ shows a composition dependence, it is only about $\frac{1}{2}$ to $\frac{3}{4}$ that of $[D_{12}]_2$. It is clear that $[D_{12}]_{app}$ represents neither $[D_{12}]_1$ or $[D_{12}]_2$, as pointed out by Burnett,[6] but the numerical results show that $[D_{12}]_{app}$ can be taken equal to the value of $[D_{12}]_2$ at a composition corresponding to a trace of the heavy component without incurring any error as large

as current experimental uncertainties involved in the direct measurement of D_{12}.

Calculations were also made on the polyatomic gas mixture N_2–CO_2, with the Lennard-Jones (12–6) potential. The results are in accord with those obtained for the noble-gas mixtures and are therefore not reported in detail.

IV. DISCUSSION

From the foregoing numerical study we conclude that $[D_{12}]_{app}$ as calculated from binary viscosity data is an accurate approximation to the true binary diffusion coefficient. If viscosity measurements on a mixture are available with an accuracy of 0.1%, the calculated $[D_{12}]_{app}$ values are accurate to 1% or better. Since diffusion coefficients are a major source of information about forces between unlike molecules, this procedure provides such information from binary viscosity data as well.

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