

## Approximate Formulas for the Viscosity and Thermal Conductivity of Gas Mixtures

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# Approximate Formulas for the Viscosity and Thermal Conductivity of Gas Mixtures

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Approximate expressions for the viscosity and thermal conductivity of gas mixtures have been derived from the rigorous kinetic theory formulas. Three levels of approximation are distinguished, with the third approximation rigorous for binary mixtures.

The first approximation for mixture viscosity is found to be very nearly equivalent to empirical expressions known heretofore. The first and second approximations for mixture conductivity have been compared with rigorous calculations for binary mixtures of nonpolar gas pairs; the first approximation has an average error of 2.6% while the second approximation reduces this error to 0.5%.

The second approximation accounts for the thermal conductivity of binary mixtures of polar and nonpolar gases. (It is assumed that the interchange of translational energy is abnormal for the polar-polar interaction.)

## INTRODUCTION

IN MANY problems involving fluid flow and heat transfer the viscosities and thermal conductivities of gas mixtures are required, often under conditions where measurement is difficult or impossible, e.g., in combustion systems.

For rough estimates, empirical methods of approximating mixture viscosities<sup>1</sup> and conductivities<sup>1,2</sup> are available. While such methods have engineering usefulness, they are not particularly accurate; they suffer the further disadvantage of being particularly suspect when extrapolated to new types of systems.

Mixing rules were derived from crude kinetic theory arguments more than half a century ago<sup>3,4</sup>; these forms provide a basis for the most reliable empirical methods in use today. Thus the viscosity equations of Buddenberg and Wilke,<sup>5</sup> and Wilke<sup>6</sup> stem from Sutherland's expression, while Lindsay and Bromley's<sup>7</sup> thermal conductivity formula is based on the equation of Wassiljewa.<sup>4</sup> These formulas include terms to characterize all pair-wise molecular interactions of the gas mixture, and are hence about the simplest forms which can be expected to have general applicability.

Rigorous kinetic theory expressions for the viscosity and monatomic thermal conductivity of gas mixtures are presented by Hirschfelder, Curtiss, and Bird<sup>8</sup> while Hirschfelder<sup>9</sup> has recently developed an Eucken-

type correction for polyatomic gas mixtures. These rigorous equations describe the viscosity and thermal conductivity of gas mixtures very well; however, the expressions are cumbersome, and calculations are tedious.

In this paper approximate formulas for the viscosity and thermal conductivity of multicomponent gas mixtures are developed from the rigorous kinetic theory expressions; three levels of approximation are defined. The formula for viscosity is found to be closely related to known empirical expressions.<sup>5,6</sup> The first and second approximations to the mixture thermal conductivity are compared with rigorous theory and with experiment for four binary systems, and with experiment for three ternary systems. Finally the conductivity equations are applied to polar-nonpolar gas mixtures.

## DERIVATION OF APPROXIMATE FORMULAS

According to Hirschfelder *et al.*,<sup>8</sup> the viscosity of a  $\nu$  component mixture is given by an expression of the form

$$\Phi = - \frac{\begin{vmatrix} 0 & x_1 & \cdots & x_\nu \\ x_1 & a_{11} & \cdots & a_{1\nu} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ x_\nu & a_{1\nu} & \cdots & a_{\nu\nu} \end{vmatrix}}{\begin{vmatrix} a_{11} & \cdots & a_{1\nu} \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ a_{1\nu} & \cdots & a_{\nu\nu} \end{vmatrix}} \quad (1)$$

If thermal diffusion is neglected, the thermal conductivity of a mixture of monatomic gases is also given by a formula of the form of Eq. (1),<sup>10</sup> in which  $\Phi$  repre-

<sup>10</sup> In reference 8, p. 537, the thermal conductivity of a mixture of monatomic gases is given by a ratio of determinants of order  $(2\nu+1)/2\nu$ . If thermal diffusion is neglected ( $\xi C^* - 1 = 0$ ), the orders of the determinants are reduced to  $(\nu+1)/\nu$ , and the ratio may be rearranged to the form of Eq. (1).

See also E. A. Mason, *J. Chem. Phys.* **28**, 1000 (1958), and Curtiss, Hirschfelder, and Bird, reference 1, p. 3, Eq. (2:2-2).

Very recently C. Muckenfuss and C. F. Curtiss (University of Wisconsin Rept. WIS-NSF-10 (April 9, 1958)) have shown that Eq. (1) is in fact an exact expression for mixture conductivity.

<sup>1</sup> L. Friend and S. B. Adler, *Proceedings of the Second Biennial Gas Dynamics Symposium, Transport Properties in Gases* (Northwestern University Press, Evanston, Illinois, 1958), p. 124.

<sup>2</sup> H. Lehmann, *Chem. Tech.* **9**, 530 (1957).

<sup>3</sup> W. Sutherland, *Phil. Mag.* **40**, 421 (1895).

<sup>4</sup> A. Wassiljewa, *Physik. Z.* **5**, 737 (1904).

<sup>5</sup> J. W. Buddenberg and C. R. Wilke, *Ind. Eng. Chem.* **41**, 1345 (1949).

<sup>6</sup> C. R. Wilke, *J. Chem. Phys.* **18**, 517 (1950).

<sup>7</sup> A. L. Lindsay and L. A. Bromley, *Ind. Eng. Chem.* **42**, 1508 (1950).

<sup>8</sup> Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), pp. 531, 537.

<sup>9</sup> J. O. Hirschfelder, *Sixth Symposium (International) on Combustion* (Reinhold Publishing Corporation, New York, 1957), p. 351, and "Generalization of the Eucken Approximation for the Heat Conductivity of Polyatomic or Chemically Reacting Gas Mixtures," Session 3, Paper 5, The International Union of Pure and Applied Chemistry and The Institution of Mechanical Engineers Joint Conference on Thermodynamic and Transport Properties of Fluids, London, July 10-12, 1957.

sents either viscosity or thermal conductivity; the  $x_i$  are the mole fractions of the constituent gases. The elements  $a_{ij}$  are different for conductivity and viscosity.

Equation (1) may be expanded as an infinite series<sup>11</sup>

$$\mathcal{P} = \sum_{i=1}^v \frac{x_i^2}{a_{ii}} - \sum_{i=1}^v \sum_{j=1, j \neq i}^v \frac{x_i x_j a_{ij}}{a_{ii} a_{jj}} + \sum_{i=1}^v \sum_{j=1, j \neq i}^v \sum_{k=1, k \neq i, j}^v \frac{x_i x_j a_{ik} a_{jk}}{a_{ii} a_{jj} a_{kk}} - \sum_{i=1}^v \sum_{j=1, j \neq i}^v \sum_{k=1, k \neq i, j}^v \sum_{l=1, l \neq i, j, k}^v \frac{x_i x_j a_{ik} a_{kl} a_{jl}}{a_{ii} a_{jj} a_{kk} a_{ll}} + \dots \quad (2)$$

Equation (1) may be approximated by the expression

$$\mathcal{P} \cong \sum_{i=1}^v \frac{x_i^2}{a_{ii}} \frac{1}{1 + \sum_{j=1, j \neq i}^v \frac{a_{ij} x_j}{a_{ii} x_i}} = \sum_{i=1}^v \frac{x_i^2}{b_i} \frac{1 + \sum_{j=1, j \neq i}^v \frac{a_{ij}}{a_{ii}}}{1 + \sum_{j=1, j \neq i}^v \frac{a_{ij} x_j}{a_{ii} x_i}} \quad (3)$$

since this equation may also be expanded as a series, with the first three terms identical to the corresponding terms of Eq. (2). Hence Eqs. (1) and (3) are identical through terms of order  $a_{ij} a_{ik}$ ; they differ only in the higher terms, beginning with the quadruple sum. In Eq. (3) a new quantity,

$$b_i \equiv a_{ii} + \sum_{j=1, j \neq i}^v a_{ij},$$

has been introduced.

In general, the  $a_{ij}$  are small compared to the  $a_{ii}$  and  $a_{jj}$ , so that as a first approximation

$$\mathcal{P}_I = \sum_{i=1}^v \frac{x_i^2}{b_i} = \sum_{i=1}^v \{\mathcal{P}_i\}_I, \quad (4)$$

where the quantity  $\{\mathcal{P}_i\}$  may be thought of as a partial viscosity or conductivity<sup>12</sup> (analogous to a partial pressure).

Although Eq. (3) is only approximate, its form is suggestive; thus, for binary mixtures *only*, the exact expression [Eq. (1)] may be written

$$\mathcal{P} = \sum_{i=1}^2 \{\mathcal{P}_i\}_I \frac{1 - \sum_{j=1, j \neq i}^2 \frac{a_{ij} x_j}{a_{ii} x_i}}{1 - \sum_{j=1, j \neq i}^2 \frac{a_{ij} b_j}{a_{ii} a_{jj} b_i}} \quad (5a)$$

Equations (3) and (5a) are very similar; if we note that  $a_{ii}/b_i \cong a_{jj}/b_j$  and that  $1 + \delta \cong (1 - \delta)^{-1}$  when  $\delta$  is small

compared to unity, Eq. (3) becomes

$$\mathcal{P} \cong \sum_{i=1}^v \{\mathcal{P}_i\}_I \frac{1 - \sum_{j=1, j \neq i}^v \frac{a_{ij} x_j}{a_{ii} x_i}}{1 - \sum_{j=1, j \neq i}^v \frac{a_{ij} b_j}{a_{ii} a_{jj} b_i}} = \sum_{i=1}^v \{\mathcal{P}_i\}_I \frac{1 - \sum_{j=1, j \neq i}^v \frac{a_{ij}}{x_i x_j} \{\mathcal{P}_j\}_I \left(1 - \sum_{k=1, k \neq j}^v \frac{a_{jk}}{x_j x_k} \{\mathcal{P}_k\}_I \frac{x_k}{x_j}\right)^{-1}}{1 - \sum_{j=1, j \neq i}^v \frac{a_{ij}}{x_i x_j} \{\mathcal{P}_j\}_I \frac{x_j}{x_i} \left(1 - \sum_{k=1, k \neq j}^v \frac{a_{jk}}{x_j x_k} \{\mathcal{P}_k\}_I \frac{x_k}{x_j}\right)^{-1}} \quad (5b)$$

Equation (5b) is exact for binary mixtures, whereas Eq. (3) is not. It seems reasonable that Eq. (5b) should also be better than Eq. (3) for mixtures of more than two components. The expression becomes considerably easier to use if the sums over  $k$  are neglected; this may be regarded as a second approximation:

$$\mathcal{P}_{II} = \sum_{i=1}^v \{\mathcal{P}_i\}_{II} = \sum_{i=1}^v \{\mathcal{P}_i\}_I C_i, \quad (6)$$

where

$$C_i = \frac{1 - \sum_{j=1, j \neq i}^v \frac{a_{ij}}{x_i x_j} \{\mathcal{P}_j\}_I}{1 - \sum_{j=1, j \neq i}^v \frac{a_{ij}}{x_i x_j} \{\mathcal{P}_j\}_I \frac{x_j}{x_i}} \quad (7)$$

Equation (5b) may then be regarded as a third approximation (rigorous for binary mixtures).

Actually, the second and third approximations are primarily of academic interest, since all the elements required for the rigorous expression [Eq. (1)] must be computed for these approximations; furthermore, a ratio of determinants of the form of Eq. (1) is relatively easy to reduce in specific numerical cases.

## VISCOSITY OF GAS MIXTURES

For the first approximation to mixture viscosity Eq. (4) becomes<sup>13</sup>

$$(\eta_{\text{mix}})_I = \sum_{i=1}^v \{\eta_i\}_I = \sum_{i=1}^v \frac{\eta_i}{1 + \sum_{j=1, j \neq i}^v \varphi_{ij} \frac{x_j}{x_i}} \quad (8)$$

where  $\{\eta_i\}_I$  is the partial viscosity of component  $i$  (1st approximation),  $\eta_i$  is the viscosity of pure component  $i$ , and

$$\varphi_{ij} = \frac{6}{5} A_{ij}^* \frac{RT}{PM_i D_{ij}}, \quad (9a)$$

<sup>11</sup> Reference 8, p. 532.

<sup>12</sup> Subscript Roman numerals are used to indicate order of approximation, as these are all approximations to the *first* approximation in the sense of Chapman (usually indicated by an Arabic numeral).

<sup>13</sup> The elements  $a_{ii}$  and  $a_{ij}$  for viscosity are identical to the elements  $H_{ii}$  and  $H_{ij}$  defined in Eqs. (8.2-26) and (8.2-27) of reference 8.

TABLE I. Viscosities of hydrogen-argon mixtures at 20°C (poise×10<sup>7</sup>).

% H <sub>2</sub>	$\eta_{\text{expt}}^a$	$\eta_{\text{Sutherland}}^b$	$\eta_I^c$	$\eta_{II}^d$	$\eta_{\text{rigorous}} (= \eta_{III})^e$
0	2211	2223	2223	2223	2223
29.42	2140	2084	2194	2141	2140
44.57	2056	1971	2148	2060	2060
65.15	1857	1736	2003	1864	1860
100	875	876	876	876	876

<sup>a</sup> Landolt-Bornstein, *Physikalisch-Chemische Tabellen*, as quoted in reference 14.

<sup>b</sup> Equations (8) and (9c), together with force constants from reference 14.

<sup>c</sup> Equations (8) and (9b).

<sup>d</sup> Equation (10).

<sup>e</sup> Reference 14.

where  $R$  is the molar gas constant,  $T$  the absolute temperature,  $P$  the pressure,  $M_i$  the molecular weight of component  $i$ , and  $D_{ij}$  is the binary diffusion coefficient between components  $i$  and  $j$ . The quantity  $A_{ij}^*$  (defined in reference 8, p. 528) is a number close to unity, whose exact value depends on the intermolecular potential.

Equation (8) is identical in form to the mixture viscosity expression originally proposed by Sutherland.<sup>3</sup> Recently Buddenberg and Wilke<sup>5</sup> and Wilke<sup>6</sup> have developed expressions for the  $\varphi_{ij}$  by semiempirical means. Equation (9a) is identical to the formula of Buddenberg and Wilke<sup>5</sup> if the quantity  $(6/5)A_{ij}^*$  is set equal to 1.385. For realistic intermolecular potentials  $A_{ij}^* \cong 1.10$ , so  $(6/5)A_{ij}^* \cong 1.32$ . The higher value found empirically by Buddenberg and Wilke probably partially corrects for systematic errors of the first approximation.

By introducing the relation between viscosity and self-diffusion coefficient,  $\eta_i = \rho_i D_i 5 / (6A_i^*)$  [reference 8, Eq. (8.2-38)], Eq. (9a) becomes

$$\varphi_{ij} = \frac{D_i A_{ij}^*}{D_{ij} A_i^*} = \frac{\lambda_i}{\lambda_{ij}}, \quad (9b)$$

where  $\lambda_i$  is the monatomic thermal conductivity of component  $i$ , and  $\lambda_{ij}$  is defined in reference 8, page 534. If the ratio  $A_{ij}^*/A_i^*$  is omitted (this ratio rarely differs from unity by more than a very few percent), Eq. (9b) is equivalent to Wilke's later expression.<sup>6</sup>

It is interesting to note, that Sutherland<sup>3</sup> originally proposed an empirical expression for the  $\varphi$ 's which is equivalent to

$$\varphi_{ij} = \frac{\lambda_i}{\lambda_{ij}} \left( \frac{M_i + M_j}{2M_j} \right)^{\frac{1}{2}}. \quad (9c)$$

The ensuing six decades have merely served to reduce the exponent on the factor involving molecular weights from  $\frac{1}{4}$  to zero!

The second approximation for the mixture viscosity is given by

$$(\eta_{\text{mix}})_{II} = \sum_{i=1}^n \{\eta_i\}_{II} = \sum_{i=1}^n \{\eta_i\}_I C_{i\eta}. \quad (10)$$

For viscosity, Eq. (7) becomes

$$C_{i\eta} = \frac{1 + \sum_{j=1, j \neq i}^n \alpha_{ij} \{\eta_j\}_I}{1 + \sum_{j=1, j \neq i}^n \alpha_{ij} \{\eta_i\}_I \frac{x_j}{x_i}}, \quad (11)$$

where

$$\begin{aligned} \alpha_{ij} &= \alpha_{ji} = \frac{2}{M_i + M_j} \frac{RT}{D_{ij}P} \left( 1 - \frac{3}{5} A_{ij}^* \right) \\ &= \frac{M_i}{M_i + M_j} \frac{\varphi_{ij}}{\eta_i} \left( \frac{5}{3A_{ij}^*} - 1 \right). \end{aligned}$$

For the third approximation, no new coefficients are required; the sums are merely formed in a more complex fashion.

An extensive comparison of these equations with experimental mixture viscosities is not warranted here, since expressions very nearly equivalent to the first approximation [Eqs. (8) and (9a) or (9b)] have been considered in references 5 and 6, while Hirschfelder, Bird, and Spotz<sup>14</sup> have carried out rigorous computations for many binary mixtures (equivalent to the third approximation).

Comparisons for one binary system (H<sub>2</sub>-A mixtures at 20°C) are shown in Table I. For this case the second approximation is almost identical to the rigorous calculation. Note that  $\eta_{\text{Sutherland}}$  and  $\eta_I$  bracket the rigorous values; hence one is tempted to propose empirically

$$\varphi_{ij} = \frac{\lambda_i}{\lambda_{ij}} \left( \frac{M_i + M_j}{2M_j} \right)^{1/8},$$

which works very well in this case. However, this procedure cannot be recommended without more extensive comparisons with experimental data.

Approximate and rigorous viscosities computed for a ternary mixture of 50% CH<sub>4</sub>, 35% N<sub>2</sub>, and 15% O<sub>2</sub>

<sup>14</sup> Hirschfelder, Bird, and Spotz, *Chem. Revs.* **44**, 205 (1949).

at 380°K are as follows<sup>15</sup>:

$$\begin{aligned}(\eta_{\text{mix}})_I &= 1790.1 \times 10^{-7} \text{ poise,} \\ (\eta_{\text{mix}})_{II} &= 1765.4 \times 10^{-7}, \\ (\eta_{\text{mix}})_{III} &= 1762.6 \times 10^{-7}, \\ (\eta_{\text{mix}})_{\text{rigorous}} &= 1761.6 \times 10^{-7}.\end{aligned}$$

It is seen that the successive approximations do indeed approach the rigorous value. However, it is almost as difficult to compute the second approximation as the rigorous value; hence the second and third approximations are of limited usefulness.

### THERMAL CONDUCTIVITY OF GAS MIXTURES

For the first approximation to the conductivity of a mixture of monatomic gases, Eq. (4) gives<sup>16</sup>

$$\lambda_{\text{mix}} = \sum_{i=1}^v \{ \lambda_{i\text{mon}} \}_I = \sum_{i=1}^v \frac{\lambda_{i\text{mon}}}{1 + \sum_{\substack{j=1 \\ j \neq i}}^v \psi_{ij} \frac{x_j}{x_i}}, \quad (12)$$

where

$$\psi_{ij} = \varphi_{ij} \left\{ 1 + \left( \frac{M_i - M_j}{M_i + M_j} \right)^2 \left( \frac{15}{4A_{ij}^*} - 1 \right) \right. \\ \left. \cdot \left[ 1 + \left( \frac{12B_{ij}^* + 5}{30 - 8A_{ij}^*} \right) \frac{M_j}{M_i - M_j} \right] \right\}. \quad (13)$$

( $B_{ij}^*$  is defined in reference 8, page 528.) Equation (12) is identical to the form originally suggested by Wassiljewa<sup>4</sup>; the empirical expression for the  $\psi_{ij}$  developed by Lindsay and Bromley<sup>7</sup> works well in many cases. It is not surprising that (unlike the case of viscosity) the empirical expression bears little relation to the complex function of molecular weights derived here [Eq. (13)].

The second approximation to the thermal conductivity of a monatomic gas mixture is

$$\lambda_{\text{mix}} = \sum_{i=1}^v \{ \lambda_{i\text{mon}} \}_{II} = \sum_{i=1}^v \{ \lambda_{i\text{mon}} \}_I C_{i\lambda} \quad (14)$$

where, from Eq. (7),

$$C_{i\lambda} = \frac{1 + \sum_{\substack{j=1 \\ j \neq i}}^v \beta_{ij} \{ \lambda_{j\text{mon}} \}_I}{1 + \sum_{\substack{j=1 \\ j \neq i}}^v \beta_{ij} \{ \lambda_{j\text{mon}} \}_I \frac{x_j}{x_i}}$$

and

$$\beta_{ij} = \beta_{ji} = \frac{M_i M_j}{(M_i + M_j)^2} \frac{1}{\lambda_{ij}} \left( \frac{55}{8A_{ij}^*} - \frac{3B_{ij}^*}{2A_{ij}^*} - 2 \right).$$

Again, the third approximation requires no new

<sup>15</sup> Calculated from elements  $H_{ii}$  and  $H_{ij}$  computed in reference 8, Table 8.4-8.

<sup>16</sup> The elements  $a_{ii}$  and  $a_{ij}$  for conductivity are  $a_{ii} = -L_{ii}^{11}/4$ ,  $a_{ij} = -L_{ij}^{11}/4$ , where  $L_{ii}^{11}$  and  $L_{ij}^{11}$  are defined in reference 8, p. 538.

coefficients, but the sums are formed in a more complex manner.

For mixtures of polyatomic gases,

$$\lambda_{\text{mix}} = \lambda_{\text{mix}} + \lambda_{\text{int}} \quad (15)$$

The term  $\lambda_{\text{mix}, \text{int}}$  (in the nature of an Eucken correction) accounts for the transport of internal energy by a diffusional mechanism. It may be computed from the following formula<sup>9</sup>:

$$\lambda_{\text{mix}, \text{int}} = \sum_{i=1}^v \frac{\lambda_{i\text{int}}}{1 + \sum_{\substack{j=1 \\ j \neq i}}^v \frac{D_i}{D_{ij}} \frac{x_j}{x_i}} \quad (16)$$

where

$$\lambda_{i\text{int}} = \lambda_{i\text{ext}} - \lambda_{i\text{mon}}. \quad (17)$$

### Comparisons for Nonpolar Gas Mixtures

Experimental and computed thermal conductivities for several nonpolar gas mixtures are compared in Tables II and III. Calculations have been carried out assuming the Lennard-Jones (6-12) potential with force constants and formulas of reference 8.

The helium-argon (Table II) and helium-argon-xenon mixtures (Table III) provide a direct test of the formulas of this paper, since these mixtures involve monatomic gases only. As in the case of gas mixture viscosities, the first approximation gives somewhat high values, while the second approximation agrees quite closely with the rigorous values for He-A and experimental values for He-A-Xe.

The mixtures involving polyatomic gases show similar trends, with the second approximation in good agreement with rigorous calculation. [The conductivities of the pure gases are indicated parenthetically in Table II, as these were not computed; rather the experimental values were used to obtain  $\lambda_{i\text{int}}$  via Eq. (17).] These computations further support the Eucken-type correction for gas mixtures derived by Hirschfelder. In this connection the benzene-argon mixtures are particularly interesting: although benzene and argon have molecular weights and thermal conductivities which are not too dissimilar, the mode of heat transport varies greatly. The benzene molecule transports three-quarters of the heat as internal energy, while the argon transfers heat as kinetic energy of translation only. The agreement between computed and experimental conductivities for this case is gratifying.

The first approximation can be brought into closer agreement with the second approximation and rigorous calculation by empirically setting  $A_{ij}^* = B_{ij}^* = 1.06$  in Eq. (13); values so computed are shown as  $\lambda_{1.06}$  in Tables II and III. This works well for mixtures involving large differences in molecular weight (He-A, He-A-Xe, H<sub>2</sub>-A, H<sub>2</sub>-CO<sub>2</sub>, He-CH<sub>4</sub>-O<sub>2</sub>), but gives only a slight improvement for other cases (C<sub>6</sub>H<sub>6</sub>-A, A-CH<sub>4</sub>-O<sub>2</sub>).

TABLE II. Thermal conductivities of binary nonpolar gas mixtures ( $\text{cal} \times 10^5 / \text{cm sec } ^\circ\text{C}$ ).

Gas pair and temperature	% of first gas	$\lambda_{\text{expt}}$	$\lambda_{1,00}^a$	$\lambda_I^b$	$\lambda_{II}^c$	$\lambda_{\text{rigorous}} (= \lambda_{III})$
He-A $0^\circ\text{C}$	0	3.89 <sup>d</sup>	3.91	3.91	3.91	3.91 <sup>e</sup>
	27.04	7.42	7.54	7.80	7.42	7.55
	45.37	10.77	11.06	11.48	10.79	11.02
	84.68	23.20	24.61	25.06	24.11	24.39
	94.61	29.39	30.60	30.83	30.31	30.46
	100	33.86	34.66	34.66	34.66	34.66
H <sub>2</sub> -A $0^\circ\text{C}$	0	3.9 <sup>f</sup>	(3.90)	(3.90)	(3.90)	(3.90) <sup>g</sup>
	9	5.5	5.41	5.50	5.43	5.45
	18	7.3	7.09	7.27	7.13	7.15
	40	12.6	12.14	12.52	12.22	12.23
	60	18.7	18.38	18.89	18.44	18.44
	80.2	27.0	27.27	27.75	27.30	27.32
	100	40.4	(40.40)	(40.40)	(40.40)	(40.40)
H <sub>2</sub> -CO <sub>2</sub> $0^\circ\text{C}$	0	3.6 <sup>f</sup>	(3.60)	(3.60)	(3.60)	(3.60) <sup>h</sup>
	10	5.1	5.03	5.11	5.04	5.05
	14.2	5.7	5.69	5.80	5.71	5.72
	25	7.7	7.58	7.78	7.61	7.63
	35.5	10.0	9.74	10.03	9.78	9.82
	50	13.5	13.43	13.83	13.47	13.50
	75	22.7	22.85	23.37	22.88	22.91
	90.1	31.5	31.92	32.30	31.93	31.95
	100	40.4	(40.40)	(40.40)	(40.40)	(40.40)
C <sub>6</sub> H <sub>6</sub> -A $78^\circ\text{C}$	0	4.85 <sup>i</sup>	(4.85)	(4.85)	(4.85)	(4.85) <sup>j</sup>
	25	4.18	4.45	4.48	4.15	4.20
	50	3.79	4.06	4.09	3.85	3.84
	75	3.58	3.72	3.74	3.64	3.61
	100	3.455	(3.455)	(3.455)	(3.455)	(3.455)

<sup>a</sup>  $\lambda_{\text{mon}}^{\text{mix}}$  computed with  $A_{ij}^* = B_{ij}^* = 1.06$ . Force constants from reference 8.

<sup>b</sup>  $\lambda_{\text{mon}}^{\text{mix}}$  from Eqs. (12) and (13).

<sup>c</sup>  $\lambda_{\text{mon}}^{\text{mix}}$  from Eq. (14).

<sup>d</sup> J. Wachsmuth, Physik. Z. 9, 235 (1908).

<sup>e</sup> Reference 8, p. 576.

<sup>f</sup> T. L. Ibbs and A. A. Hirst, Proc. Roy. Soc. (London) A123, 134 (1929).

<sup>g</sup> Calculation of  $\lambda_{\text{mon}}^{\text{mix}}$  of reference 8, p. 578, using  $\lambda_{\text{int}}^{\text{mix}}$  calculated according to reference 9.

<sup>h</sup> Reference 9, Table 11.

<sup>i</sup> Reference 22. These figures were read from a graph, and may be somewhat in error.

<sup>j</sup> Computed this paper, as  $\lambda_{III}$ .

 TABLE III. Thermal conductivities of ternary nonpolar gas mixtures ( $\text{cal} \times 10^5 / \text{cm sec } ^\circ\text{C}$ ).

Gases and temperature	1st Gas	% of 2nd Gas	3rd Gas	$\lambda_{1,00}^a$	$\lambda_I^a$	$\lambda_{II}^a$	$\lambda_{\text{expt}}$
He-A-Xe $38^\circ\text{C}$	11.38	14.95	73.67	2.857	2.969	2.861	2.836 <sup>b</sup>
	19.67	18.00	62.33	4.016	4.205	4.024	4.004
	39.01	36.75	24.24	8.53	8.93	8.42	8.45
	32.02	60.65	7.33	8.54	8.89	8.37	8.43
	68.01	18.80	13.19	16.63	17.26	16.47	16.62
He-CH <sub>4</sub> -O <sub>2</sub> $0^\circ\text{C}$	74.3	6.0	19.7	21.0	21.5	20.1	20.0 <sup>c</sup>
	71.2	10.0	18.8	20.1	20.5	19.1	19.5
	68.4	13.5	18.1	19.3	19.7	18.2	18.6
A-CH <sub>4</sub> -O <sub>2</sub> $0^\circ\text{C}$	75.1	5.0	19.9	4.38	4.39	4.40	4.59 <sup>c</sup>
	71.2	10.0	18.8	4.48	4.50	4.50	4.71
	67.7	14.4	17.9	4.57	4.60	4.59	4.91

<sup>a</sup> See references a, b, and c, Table II.

<sup>b</sup> S. C. Saxena, J. Chem. Phys. 25, 360 (1956).

<sup>c</sup> Clingman, Brokaw, and Pease, *Fourth Symposium (International) on Combustion* (Williams and Wilkins Company, Baltimore, 1953), p. 310.

### Comparisons for Mixtures of Polar and Nonpolar Gases

In order to discuss the thermal conductivity of mixtures of polar and nonpolar gases, it is necessary first to consider briefly the relation between viscosity and thermal conductivity for pure gases

$$\lambda = \frac{\eta}{M} (f_{\text{trans}} C v_{\text{trans}} + f_{\text{int}} C v_{\text{int}}) \\ = \lambda_{\text{mon}} + \lambda_{\text{int}}, \quad (18)$$

where  $C v_{\text{trans}}$  and  $C v_{\text{int}}$  are molar heat capacities associated with translational and internal energy, respectively. For spherical nonpolar molecules  $f_{\text{trans}} = 2.5$ . Chapman and Cowling<sup>17</sup> observed that the transport of internal energy takes place by a diffusion mechanism, which leads to  $f_{\text{int}} = D\rho/\eta = (6/5) A^* \cong 1.32$ . Vines and Bennett<sup>18</sup> have studied the thermal conductivities of nonpolar organic vapors and conclude that with increasing temperature  $f_{\text{int}} \rightarrow D\rho/\eta$ .

With polar molecules experimental thermal conductivities are smaller than values computed from Eq. (18) assuming  $f_{\text{trans}} = 2.5$  and  $f_{\text{int}} \cong 1.2$  to 1.3; Vines and Bennett follow Schaefer<sup>19</sup> in suggesting that for polar molecules  $f_{\text{trans}} < 2.5$ .

To compute  $\lambda_{\text{mix,mon}}$  for polar-nonpolar mixtures by means of Eqs. (12), (13), and (14),  $\lambda_{p\text{mon}}$ , the monatomic conductivity of the polar constituent is required. This has been taken as [see Eq. (18)]

$$\lambda_{p\text{mon}} = \lambda_{p\text{expt}} - f_{\text{int}} \frac{C v_{\text{int}} \eta_p}{M_p} \quad (19)$$

To compute  $\lambda_{\text{mix,int}}$  [Eq. (16)] the ratio  $D_p/D_{np}$ , involving the self-diffusion coefficient of the polar molecule, is required. ( $D_{np}$  is the binary diffusion coefficient between polar and nonpolar molecules.) While there are no data on self-diffusion coefficients for polar molecules, one would expect the polar coefficient of self-diffusion to be related to viscosity in the usual fashion, so that

$$\frac{D_p}{D_{np}} = \frac{15}{4} \frac{R}{M} \frac{\eta_p}{\lambda_{np}} \frac{A_p^*}{A_{np}^*} \cong \frac{15}{4} \frac{R}{M} \frac{\eta_p}{\lambda_{np}} \quad (20)$$

(For consistency the ratio  $D_p/D_{np}$  has been approximated as  $\lambda_{n\text{mon}}/\lambda_{np}$ .) Experimental and calculated thermal conductivities for six polar-nonpolar gas pairs are compared in Fig. 1. (Calculated curves are for  $\lambda_{\text{mix,II}}$ .) Polar gases involved are water,<sup>20</sup> ammonia,<sup>21</sup>

methanol,<sup>22</sup> and acetone.<sup>22</sup> (For the ammonia mixtures constants used were  $\eta_{\text{NH}_3} = 9.95 \times 10^{-5}$  poise,  $C v_{\text{int}} = 3.56$  cal/mole °K,  $f_{\text{int}} = 1.23$ ; for the other mixtures corresponding quantities were from reference 22, Table I.) The quantity  $\lambda_{np}$  has been adjusted to fit the experimental data (this will be discussed later). In general the forms of the conductivity-concentration curves in Fig. 1 are satisfactory; maximum deviations are about 1%. Thus the equations for the thermal conductivity of binary mixtures adequately described the behavior of polar-nonpolar mixtures if it is assumed that  $f_{\text{trans}}$  is abnormally low for polar molecules.

Values of  $\lambda_{np}$  required to fit the experimental data are shown in Table IV. It is possible to compute  $\lambda_{np}$  from the force constants  $\sigma_{np}$  and  $\epsilon_{np}$  characteristic of the polar-nonpolar interaction; these in turn can in principle be computed from the force constants for the pure polar and nonpolar constituents.<sup>23</sup> Force constants for the polar constituents are available from two sources. First, there are constants obtained by fitting PVT data to the Stockmayer potential.<sup>24</sup> The Stockmayer potential is a fairly realistic one for polar molecules, but for PVT data the angle-dependent dipole inter-

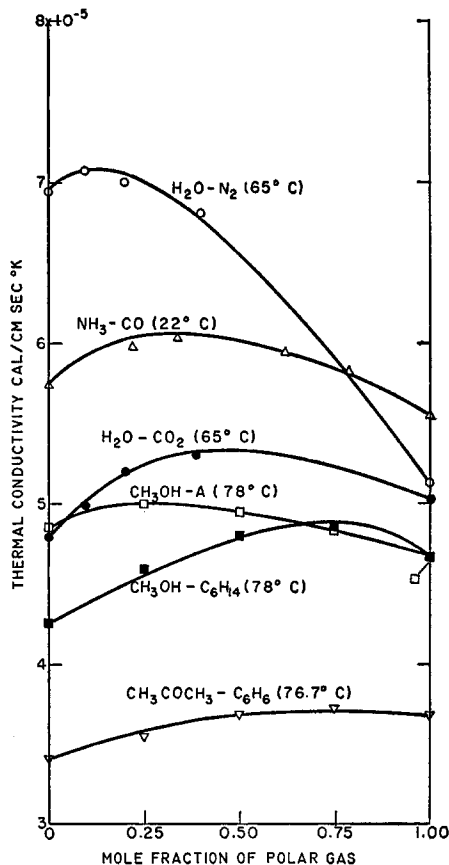


FIG. 1. Experimental and computed thermal conductivities of polar-nonpolar gas mixtures.

<sup>17</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1939).

<sup>18</sup> R. G. Vines and L. A. Bennett, *J. Chem. Phys.* **22**, 360 (1954).

<sup>19</sup> K. Schaefer, *Z. physik. Chem. (Leipzig)* **B53**, 149 (1943).

<sup>20</sup> D. L. Timrot and N. B. Vargaftik, *Transactions Fourth World Power Conference III* (Lund-Humphries, London, 1952), p. 1642.

<sup>21</sup> H. Gruss and H. Schmick, *Wiss. Veroffentl. Siemens-Konzern* **7**, 202 (1928).

<sup>22</sup> L. A. Bennett and R. G. Vines, *J. Chem. Phys.* **23**, 1587 (1955).

<sup>23</sup> Reference 8, p. 600.

<sup>24</sup> J. S. Rowlinson, *Trans. Faraday Soc.* **45**, 974 (1949). See also reference 8, p. 214.

TABLE IV. Comparison of experimental and computed  $\lambda_{np}$  values.

Gas pair	T, °C	$\lambda_{np}$ , cal $\times 10^3$ /cm sec °C		
		Experimental	Calc Krieger	Calc Stockmayer
H <sub>2</sub> O—N <sub>2</sub>	65	5.7	6.50	6.54
H <sub>2</sub> O—CO <sub>2</sub>	65	4.2	4.78	4.48
CH <sub>3</sub> COCH <sub>3</sub> —C <sub>6</sub> H <sub>6</sub>	76.7	1.03	1.12	1.17
CH <sub>3</sub> OH—A	78	3.9	4.01	5.04
CH <sub>3</sub> OH—C <sub>6</sub> H <sub>14</sub>	78	1.53	1.51	1.60
NH <sub>3</sub> —CO	22	5.0	5.33	5.91
NH <sub>3</sub> —H <sub>2</sub>	20	17.9 <sup>a</sup>	18.1	21.6
NH <sub>3</sub> —N <sub>2</sub>	20	5.16 <sup>a</sup>	5.33	5.91
NH <sub>3</sub> —O <sub>2</sub>	20	5.32 <sup>a</sup>	5.38	5.96
NH <sub>3</sub> —C <sub>2</sub> H <sub>4</sub>	20	3.58 <sup>a</sup>	3.96	4.14

<sup>a</sup> Computed from experimental force-constants obtained from mixture viscosity in reference 26.

action is of overriding importance; computed molecular diameters are abnormally small. A second set of force constants for polar molecules has been obtained by fitting an approximate angle-independent potential to viscosity data.<sup>25</sup> Viscosity data are not so strongly influenced by the dipole interactions, but the assumed potential is less realistic. Values of  $\lambda_{np}$  calculated using force constants from the Stockmayer and angle-independent potentials ( $\lambda_{np}$  Stockmayer and  $\lambda_{np}$  Krieger) are also shown in Table IV. The experimental values are, with one exception, lower than those computed by either scheme.

A similar trend is discernible from studies of the viscosities of polar-nonpolar gas mixtures. Hirschfelder, Bird, and Spatz<sup>26</sup> analyzed data on the viscosity of mixtures of ammonia with hydrogen, nitrogen, oxygen, and ethylene over a range of temperature; in this manner they obtained what may be called experimental values of  $\sigma_{np}$  and  $(\epsilon/k)_{np}$ . Values of  $\lambda_{np}$  for these gas pairs at 20°C, computed from the experimental force constants, are also shown in Table IV; these values are again lower than those computed with polar molecule force constants from the Stockmayer and angle-independent potentials.

The  $\lambda_{np}$  values from the approximate angle-independent potential are closest to the experimental values. The interaction between polar and nonpolar molecules is essentially of a nonpolar nature; that is, strongly

affected by molecular size and the inverse 6th power attractive potential, and only weakly affected by the polarity of the polar molecule. It is perhaps not surprising then, that force constants from viscosity more nearly reflect the "true" sizes of polar molecules, since the polar interactions are not as important as they are for equation-of-state data.

## SUMMARY

Approximate formulas for the viscosity and thermal conductivity of gas mixtures have been derived from the rigorous kinetic theory expressions. Three levels of approximation are defined; the third approximation is identical to the rigorous expression for binary mixtures but remains approximate for mixtures of more than two components.

The first approximation for mixture viscosities is equivalent to a formula derived semiempirically heretofore. The viscosity formulas have not been extensively tested; for one case (H<sub>2</sub>—A, 20°C) the first approximation deviated from the rigorous calculation by an average error of +4.8%, while the average error for the second approximation was less than +0.1%.

The formulas for mixture thermal conductivities, which are new, were compared with rigorous calculations for 19 mixtures of four nonpolar gas pairs. The first approximation had an average error of +2.6%, with a maximum error of 6.7%; the second approximation reduced the average error to 0.5% and reduced the maximum error to 2.1%. An empirical alteration of the first approximation gave substantial improvement for mixtures of light and heavy gases (e.g., He—A) but scant improvement for benzene-argon mixtures. Average error was 1.2%. (The rigorous calculations had an average error from experiment of 1.6%.) The approximations were compared with experimental data for three ternary systems and similar trends were noted.

The second approximation for the thermal conductivity of binary gas mixtures accounts for the behavior of polar-nonpolar gas pairs if it is assumed that the interchange of translational energy is abnormal for the polar-polar interaction. Because there are no realistic force constants for polar molecules it was necessary to select values of  $\lambda_{np}$  (characteristic of the polar-nonpolar interaction) to fit the experimental data. (Experimental  $\lambda_{np}$  values were consistently lower than computed values.)

<sup>25</sup> F. J. Krieger, Proj. RAND Report RM-646, July 1, 1951.

<sup>26</sup> Hirschfelder, Bird, and Spatz, Trans. Am. Soc. Mech. Engrs. 71, 921 (1), 949.