

CONCENTRATION DEPENDENCE OF THE VISCOSITY  
FOR BINARY GAS MIXTURES

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UDC 533.16

The rigorous kinetic theory is used to relate the thermal diffusion to the viscosity.

The concentration dependence of the viscosity for the gas mixture is of practical and theoretical interest; this is due partly to the need to monitor and control viscosities in technical processes, and also because one needs to have available general molecular-kinetic trends for the viscosity in relation to component concentration and temperature

An error of 2-3% in measurement of the viscosity does little to distort the concentration dependence of the viscosity for mixtures, and such experimental results can be used to deduce the general trends in the concentration dependence (Table 1).

Thermal diffusion has a marked influence on the mechanism of heat transfer in gas mixture [18], so it is of interest to examine the relationship for momentum transfer in gas mixtures. It has been shown [15] that thermal diffusion arises in an apparatus used for viscosity determination, and this can distort the results, so a correction has to be made for thermal diffusion in order to obtain accurate viscosities.

The experimental evidence on viscosity as a function of concentration for gas mixtures shows that the maximum in the relationship arises when helium or hydrogen is mixed with heavier molecules [23] (Tables 2 and 3). On the other hand, the viscosities of mixtures of He-Xe, He-Ar, and He-Kr have maxima as functions of concentration (the mass ratios of the components are small), while the concentration dependence of the viscosity for Ne-Xe has only an inflection.

An attempt has been made [17] to explain the maximum for CH<sub>4</sub>-NH<sub>3</sub> in terms of the variable sign of the thermal-diffusion constant  $\alpha_T$  as a function of concentration. Here we consider an analytical relationship between the viscosity and the thermal diffusion.

We use a relationship of [19] for the viscosity of a gas mixture:

$$\frac{1}{\eta} = \frac{X_{\eta} + Y_{\eta}}{1 + Z_{\eta}}, \quad (1)$$

TABLE 1. Deviations of Observed Concentrations for Maximum Viscosity Dependence from Theoretical Ones

Mixture	T, °K	$\frac{\eta_{\max, \text{exp}}}{\eta_{\max, \text{exp}}}$	$\frac{x_{\max, \text{exp}}}{x_{\max, \text{exp}}}$
He - Ar	293-373	0,99	0,81
He - Kr	293	0,98	0,96
He - Xe	293-550	0,99	0,95
H <sub>2</sub> - CH <sub>4</sub>	293-523	1,00	1,26
H <sub>2</sub> - HCl	294-523	1,00	1,31
CH <sub>4</sub> - NH <sub>3</sub>	288	0,96	1,16

Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 23, No. 6, pp. 1043-1049, December, 1972. Original article submitted June 13, 1972.

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TABLE 2. Mixtures with Maximum Viscosity

Mixture	$M_1/M_2$	$T, ^\circ\text{K}$	$\eta_1/\eta_2$ , $T=293^\circ\text{K}$	$\delta_1$	$\delta_2$	$X_{1\text{max}}^*$ , $T=293-300^\circ\text{K}$	Reference
H <sub>2</sub> —Xe	0,0152	293—550	0,39	0	0	0,26	[8]
H <sub>2</sub> —SO <sub>2</sub>	0,0314	290—472	0,703	0	1,61	0,75	[7]
He—Xe	0,0348	293—550	0,86	0	0	0,75	[8]
H <sub>2</sub> —CO <sub>2</sub>	0,0455	288—550	0,6	0	0	0,3	[4, 1]
H <sub>2</sub> —C <sub>3</sub> H <sub>8</sub>	0,0455	300—550	1,1	0	0	0,83	[4, 16]
H <sub>2</sub> —N <sub>2</sub> O	0,046	300—550	0,6	0	0,14	0,15	[4]
H <sub>2</sub> —C <sub>3</sub> H <sub>6</sub>	0,0476	313—373	1,05	0	0	0,78	[20]
He—Kr	0,0477	273—300	0,788	0	0	0,64	[12, 13]
H <sub>2</sub> —HCl	0,055	294—523	0,63	0	1,48	0,4	[6]
H <sub>2</sub> —C <sub>2</sub> H <sub>6</sub>	0,0668	293—623	0,96	0	0	0,7	[3, 20]
H <sub>2</sub> —NO	0,067	284	0,465	0	0,07	0,05	[21]
H <sub>2</sub> —C <sub>2</sub> H <sub>4</sub>	0,0715	285	0,87	0	0	0,6	[1]
H <sub>2</sub> —C <sub>2</sub> H <sub>2</sub>	0,076	293—373	0,84	0	0	0,65	[20]
He—Ar	0,1	293—373	0,88	0	0	0,55	[12, 13]
H <sub>2</sub> —NH <sub>3</sub>	0,118	285—523	0,88	0	1,46	0,55	[6, 1]
H <sub>2</sub> —CH <sub>4</sub>	0,128	293—523	0,805	0	0	0,3	[3, 20]
NH <sub>3</sub> —C <sub>2</sub> H <sub>4</sub>	0,605	285—523	0,93	0	0	0,5	[6, 1]
HCl—CO <sub>2</sub>	0,83	291	0,97	1,46	0	0,32	[2]
CH <sub>4</sub> —NH <sub>3</sub>	0,94	288	1,092	0	1,46	0,8	[17]

TABLE 3. Mixtures with Maximum Viscosity

Mixture	$M_1/M_2$	$T, ^\circ\text{K}$	$\delta_1$	$\delta_2$	$\eta_1/\eta_2$ at $T=293^\circ\text{K}$	Reference
H <sub>2</sub> —N <sub>2</sub> O	0,0455	300—550	0	0,14	0,602	[4]
H <sub>2</sub> —O <sub>2</sub>	0,0624	300—550	0	0	0,435	[9]
H <sub>2</sub> —N <sub>2</sub>	0,0713	286—292	0	0	0,495	[21, 10]
H <sub>2</sub> —CO	0,0713	284—293	0	0,112	0,498	[21, 10]
H <sub>2</sub> —Ne	0,1	290	0	0	0,279	[10]
CH <sub>4</sub> —C <sub>3</sub> H <sub>8</sub>	0,364	293—523	0	0	1,36	[3]
CH <sub>4</sub> —CO <sub>2</sub>	0,364	298	0	0	0,743	[11]
NH <sub>3</sub> —O <sub>2</sub>	0,530	288	1,46	0	1,538	[5]
CH <sub>4</sub> —C <sub>2</sub> H <sub>6</sub>	0,533	293—523	0	0	1,19	[3]
NH <sub>3</sub> —air	0,585	288	1,46	0	0,6	[2]
NH <sub>3</sub> —N <sub>2</sub>	0,609	293—523	1,46	0	0,568	[5]
air—CO <sub>2</sub>	0,66	290	0	0	1,24	[2]
C <sub>2</sub> H <sub>6</sub> —C <sub>3</sub> H <sub>8</sub>	0,682	293—523	0	0	1,14	[3]
CO <sub>2</sub> —SO <sub>2</sub>	0,69	289	0	1,61	1,18	[2]
C <sub>2</sub> H <sub>4</sub> —Ar	0,7	298	0	0	0,455	[11]
air—HCl	0,8	290	0	1,48	1,24	[2]
air—H <sub>2</sub> S	0,85	290	0	1,48	1,43	[2]
CO—SO <sub>2</sub>	0,875	300—500	0,112	0	0,865	[9]
N <sub>2</sub> —O <sub>2</sub>	0,875	300—500	0	0	0,87	[9]
C <sub>2</sub> H <sub>4</sub> —O <sub>2</sub>	0,88	293—373	0	0	0,5	[9]
CO—C <sub>2</sub> H <sub>4</sub>	1	300—500	0,112	0	1,75	[9]
CO—N <sub>2</sub>	1	300—500	0,112	0	0,98	[9]
CO <sub>2</sub> —C <sub>3</sub> H <sub>8</sub>	1	300—550	0	0	1,84	[4]
CO <sub>2</sub> —N <sub>2</sub> O	1	300—550	0	0,14	1,005	[4]
N <sub>2</sub> —C <sub>2</sub> H <sub>4</sub>	1	300—550	0	0	1,75	[9]
N <sub>2</sub> O—C <sub>3</sub> H <sub>8</sub>	1	330—550	0,14	0	1,83	[4]

where

$$X_\eta = \frac{x_1^2}{\eta_1} + \frac{2x_1x_2}{\eta_{12}} + \frac{x_2^2}{\eta_2},$$

$$Y_\eta = \frac{3}{5} A_{12}^* \left[ \frac{x_1^2}{\eta_1} \cdot \frac{M_1}{M_2} + \frac{2x_1x_2}{\eta_{12}} \cdot \frac{(M_1 + M_2)^2}{4M_1M_2} \cdot \frac{\eta_{12}^2}{\eta_1\eta_2} + \frac{x_2^2}{\eta_2} \cdot \frac{M_2}{M_1} \right],$$

$$Z_\eta = \frac{3}{5} A_{12}^* \left\{ x_1^2 \frac{M_1}{M_2} + 2x_1x_2 \left[ \frac{(M_1 + M_2)^2}{4M_1M_2} \left( \frac{\eta_{12}}{\eta_1} + \frac{\eta_{12}}{\eta_2} \right) - 1 \right] + x_2^2 \frac{M_2}{M_1} \right\},$$

$$\eta_{12} = \frac{5}{3} \frac{M_1M_2}{M_1 + M_2} \cdot \frac{pD_{12}}{A_{12}^*RT},$$

and  $D_{12}$  is the mutual diffusion coefficient.

Equation (1) may be put in the form  $\eta = f(pD_{12}/T)$  as follows [22]:

$$\left( \frac{pD_{12}}{T} \right)^2 aT^2 + \frac{pD_{12}}{T} (b + A_{12}^*c)T + A_{12}^*d = 0, \quad (2)$$

where

$$a = \frac{(x_1 x_2)^2}{\eta_1 \eta_2} (\eta - \eta_1 - \eta_2),$$

$$b = \frac{2x_1 x_2 RT}{(M_1 + M_2) \eta_1 \eta_2} [\eta (x_1^2 \eta_2 + x_2^2 \eta_1) - \eta_1 \eta_2],$$

$$c = \frac{6x_1 x_2 RT [\eta (x_1^2 M_1^2 \eta_2 + x_2^2 M_2^2 \eta_1) - (x_1 M_1 - x_2 M_2)^2 \eta_1 \eta_2]}{5(M_1 + M_2) M_1 M_2 \eta_1 \eta_2},$$

$$d = \frac{3(2x_1 x_2 RT)^2}{5M_1 M_2} \eta.$$

Then

$$\eta = \frac{\left(\frac{\rho D_{12}}{T}\right)^2 TKt + \frac{\rho D_{12}}{T} l(1 - \alpha\theta)}{\left(\frac{\rho D_{12}}{T}\right)^2 TK - \frac{\rho D_{12}}{T} l(f + \alpha\psi) + \frac{\alpha}{T} \bar{\rho}}, \quad (3)$$

where

$$l = \frac{2x_1 x_2 RT}{M_1 + M_2}, \quad f = \frac{x_1^2}{\eta_1} + \frac{x_2^2}{\eta_2},$$

$$\psi = \frac{M_1}{M_2} \cdot \frac{x_1^2}{\eta_1} + \frac{M_2}{M_1} \cdot \frac{x_2^2}{\eta_2}, \quad \theta = \frac{M_2}{M_1} \left( x_1 \frac{M_1}{M_2} + x_2 \right)^2,$$

$$\alpha = \frac{3}{5} A_{12}^*, \quad \bar{\rho} = \frac{(2x_1 x_2 RT)^2}{M_1 M_2}, \quad K = \frac{(x_1 x_2)^2}{\eta_1 \eta_2}, \quad t = \eta_1 + \eta_2.$$

We consider a mixture of polyatomic gases. The internal degrees of freedom will be identified with chemical reactions. We write the expression for the heat flux in a coordinate system moving with the mean velocity of a molecule:

$$\mathbf{q} = -\lambda \nabla T + \frac{kT}{n} \sum_{ij} \frac{n_j D_i^f}{m_i D_{ij}} (\bar{\mathbf{v}}_i - \bar{\mathbf{v}}_j). \quad (4)$$

The diffusion velocity of a molecule of the  $i$ -th component is [19] given by

$$\bar{\mathbf{v}}_i = \frac{n^2}{n_i \rho} \sum_j m_j D_{ij} \mathbf{d}_j - \frac{D_i^f}{n_i m_i} \frac{\partial \ln T}{\partial \mathbf{r}}, \quad (5)$$

where the vector  $\mathbf{d}_j$  is as follows in the absence of external forces and gradients

$$\mathbf{d}_j = \frac{\partial}{\partial \mathbf{r}} \cdot \frac{n_j}{n}. \quad (6)$$

We use (5) and (6) to put the second term in (4) in the form

$$\frac{kT}{n} \sum_{ij} \frac{n_j D_i^f}{m_i D_{ij}} (\bar{\mathbf{v}}_i - \bar{\mathbf{v}}_j) = -nkT \sum_i \frac{D_i^f}{n_i m_i} \left[ \frac{d}{dT} \cdot \frac{n_i}{n} - \frac{1}{T} \sum_j \frac{n_i n_j}{n^2 D_{ij}} \left( \frac{D_j^f}{n_j m_j} - \frac{D_i^f}{n_i m_i} \right) \right] \frac{\partial T}{\partial \mathbf{r}}, \quad (7)$$

and then (7) enables us to put (4) in the form

$$\mathbf{q} = -(\lambda + \lambda_{DT}) \frac{\partial T}{\partial \mathbf{r}}, \quad (8)$$

where

$$\lambda_{D^T} = nkT \sum_i \frac{D_i^T}{n_i m_i} \cdot \frac{dx_i}{dT} - \frac{k^2 T}{\rho} \sum_{i,j} \frac{D_i^T}{m_i D_{ij}} \left( \frac{D_j^T}{m_j} - \frac{x_j}{x_i} \cdot \frac{D_i^T}{m_i} \right), \quad (9)$$

or for a binary mixture

$$\lambda_{D^T} = \alpha_T \frac{\rho D_{12}}{T} \left( T \frac{dx_1}{dT} + k_T \right). \quad (10)$$

Then

$$\frac{\rho D_{12}}{T} = \frac{\lambda_{D^T}}{\alpha_T \left( T \frac{dx_1}{dT} + k_T \right)},$$

where

$$\alpha_T = \frac{kT D_1^T}{\rho D_{12}} \frac{x_1 m_1 + x_2 m_2}{x_1 x_2 m_1 m_2}.$$

Then (3) and (10) enable us to write

$$\eta = \frac{\frac{\lambda_{D^T}^2}{\alpha_T^2 \left( T \frac{dx_1}{dT} + k_T \right)} TKl + \frac{\lambda_{D^T}}{\alpha_T \left( T \frac{dx_1}{dT} + k_T \right)} l(1 - \alpha\theta)}{\frac{\lambda_{D^T}}{\alpha_T^2 \left( T \frac{dx_1}{dT} + k_T \right)^2} TK - \frac{\lambda_{D^T}}{\alpha_T \left( T \frac{dx_1}{dT} + k_T \right)} l \left( f + \alpha\psi \right) + \frac{\alpha}{T} \tilde{p}} \quad (11)$$

or, transferring in (11) to symbols in terms of known quantities, we get

$$\eta = \left\{ \eta_1 + \eta_2 + \frac{2\eta_1 \eta_2 \alpha_T \left( T \frac{dx_1}{dT} + k_T \right) R}{\lambda_{D^T} x_1 x_2 (M_1 + M_2)} \left[ 1 - \frac{3}{5} A_{12}^* \left( \frac{M_1}{M_2} \right)^{1/2} x_1 + \left( \frac{M_1}{M_2} \right)^{-1/2} x_2 \right]^2 \right\} \left\{ 1 - \frac{2\alpha_T \left( T \frac{dx_1}{dT} + k_T \right) R}{\lambda_{D^T} x_1 x_2 (M_1 + M_2)} \left\{ x_1^2 \eta_2 \left( 1 + \frac{3}{5} A_{12}^* \frac{M_1}{M_2} \right) + x_2^2 \eta_1 \left( 1 + \frac{3}{5} A_{12}^* \frac{M_2}{M_1} \right) \right\} + \frac{12\eta_1 \eta_2 \alpha_T^2 \left( T \frac{dx_1}{dT} + k_T \right)^2}{5\lambda_{D^T}^2 M_1 M_2 A_{12}^{*-1} R^{-2}} \right\}^{-1} \quad (12)$$

Then (12) shows that the viscosity of a gas mixture is determined by the thermal diffusion constant  $\alpha_T$ , the thermal diffusion ratio  $k_T$ , and the thermal conductivity due to thermal diffusion  $\lambda_{DT}$ .

We consider the case of a mixture for which  $M_1 \ll M_2$ ; for convenience we put (1) in the following form [17]:

$$\eta = \eta_1 x_1 + \eta_2 x_2 + \frac{(R_1 x_1 + R_2 x_2) x_1 x_2}{\frac{1}{\eta_1} P_{11} x_1^2 + \frac{2}{\eta_{12}} P_{12} x_1 x_2 + \frac{1}{\eta_2} P_{22} x_2^2}, \quad (13)$$

where

$$P_{ii} = 1 + \frac{3}{5} A_{ij}^* \frac{M_i}{M_j}, \quad P_{ij} = 1 + \frac{3}{5} A_{ij}^* \frac{\eta_{ij}^2}{4M_i M_j \eta_i \eta_j},$$

$$R_i = \left( 1 - \frac{\eta_j}{\eta_i} \right) P_{ii} + 2 \left[ 1 - \frac{\eta_i}{\eta_{ij}} + \frac{3}{5} A_{ij}^* \left( \frac{\eta_{ij}}{4M_i M_j \eta_i} - 1 \right) \right],$$

$$i \neq j; \quad i = 1, 2; \quad j = 1, 2.$$

To examine the viscosity as a function of composition we have to determine the signs of the derivatives  $(d\eta/dx_1)_{x_1 \rightarrow 0}$  and  $(d\eta/dx_1)_{x_1 \rightarrow 1}$ ; it is readily shown that

$$\left( \frac{d\eta}{dx_1} \right)_{x_1 \rightarrow 0} = \frac{1}{2} \left[ 1 - \frac{20}{3A_{12}^*} \left( \frac{\eta_2}{\eta_{12}} \right)^2 \frac{M_1}{M_2} \right] \eta_{12}, \quad (14)$$

$$\left(\frac{d\eta}{dx_1}\right)_{x_1 \rightarrow 1} = -\frac{3}{10} A_{12}^* \frac{M_2}{M_1} \eta_{12} < 0 \quad (15)$$

or

$$\begin{aligned} \left(\frac{d\eta}{dx_1}\right)_{x_1 \rightarrow 0} &= \frac{1}{2} \left[ 1 - 4 \frac{5}{3A_{12}^*} \left\{ \frac{\eta_2 R (M_1 + M_2) A_{12}^* \alpha_T \left( T \frac{dx_1}{dT} + k_T \right)}{\frac{5}{3} M_1 M_2 \lambda_{D^T}} \right\}^2 \right. \\ &\quad \times \frac{M_1}{M_2} \frac{5}{3} \cdot \frac{M_1 M_2}{A_{12}^* (M_1 + M_2)} \cdot \frac{\lambda_{D^T}}{\alpha_T \left( T \frac{dx_1}{dT} + k_T \right) R} \\ &\quad \left. = \frac{1}{2} \cdot \frac{M_2 M_1 \lambda_{D^T}^2 - 4\eta_2^2 \alpha_T^2 \left( T \frac{dx_1}{dT} + k_T \right)^2 R^2}{\alpha \lambda_{D^T} \alpha_T \left( T \frac{dx_1}{dT} + k_T \right) R M_2} \right], \end{aligned} \quad (16)$$

where

$$\alpha = \frac{3}{5} A_{12}^*.$$

We assume that  $dx_1/dT = 0$  for a mixture of monatomic gases; it is clear that a maximum will exist in the concentration dependence of the viscosity if

$$M_1 \lambda_{D^T}^2 > 4\eta_2^2 \alpha_T^2 \alpha \left( T \frac{dx_1}{dT} + k_T \right)^2 R^2$$

or

$$\lambda_{D^T} > 2\eta_2 \alpha_T \left( T \frac{dx_1}{dT} + k_T \right) \left( \frac{\alpha}{M_1 M_2} \right)^{1/2}.$$

Then this maximum is substantially dependent on the thermal diffusion separation and

$$\eta_2 < \frac{\lambda_{D^T}}{2\alpha_T \left( T \frac{dx_1}{dT} + k_T \right) R} \left( \frac{M_1 M_2}{\alpha} \right)^{1/2}. \quad (17)$$

The Chapman—Enskog theory predicts that there will be such a maximum for gases with approximately equal molecular masses and equal viscosities for the pure component, including a maximum for  $H_2-N_2O$ ; experiment does not confirm this for the latter mixture, nor does it predict the minimum viscosity for an  $N_2O-CO_2$  mixture, or a maximum for  $HCl-CO_2$  and  $NH_3-C_2H_4$ .

The theoretical results deviate from experiment because it is not always justified to use the Chapman—Enskog theory for mixtures of polyatomic gases. The formula for the viscosity of a mixture of polyatomic gases takes the same form as that for a mixture of monatomic gases, but the values of  $A_{12}^*$  differ for these cases [14].

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