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<td>Hongo, Masaru; Iwasaki, Hiroji</td>
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<td>Citation</td>
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VISCOSITY OF HYDROGEN AND OF HYDROGEN-AMMONIA MIXTURES UNDER PRESSURES*

BY MASARU HONGO AND HIROJI IWASAKI

The viscosity of gaseous hydrogen and of gaseous hydrogen-ammonia mixtures of four different ratios was measured using an oscillating disk-type viscometer at temperatures of 25, 50, 75, and 100°C, and in the pressure range up to about \(120 \times 10^5\) Pa for hydrogen and up to the vicinity of the saturated vapor pressure of ammonia for hydrogen-ammonia mixtures. The accuracy of the measurements is estimated to be within \(\pm 0.3\%\).

In the calculation of the gas viscosity of dilute binary mixtures based on Chapman-Enskog's theory, a modification of the combination rule using the critical compressibility factor was presented. The calculated viscosity values obtained by applying the critical compressibility factor were in better agreement with the experimental ones than the original Chapman-Enskog's theoretical ones.

The initial density dependence of the viscosity of hydrogen-ammonia mixtures, i.e., \(n_0^{-1}(\partial \eta/\partial n)\to 0\), increased with an increase in temperature and in the mole fraction of hydrogen as in the case of the nitrogen-ammonia system, where \(\eta\) is the viscosity of a gas, \(\eta_\infty\) is the viscosity extrapolated to zero density, and \(n\) is density. Further, it may be concluded that the nonpolar molecules of larger molecular weight disturb more strongly the dimerization of polar molecules than those of smaller molecular weight.

Introduction

Among the transport coefficients of a gas, on consideration of the molecular theory of gases the viscosity is an important physical property because it can be measured very precisely. The accurate experimental values of the viscosity of gaseous mixtures under various pressures are useful to obtain some information about intermolecular interactions and contribute to the theoretical development for dense gaseous mixtures. In recent years accurate measurements of the gas viscosity at high pressure or at high temperature have been made, but the studies about the viscosity of gaseous mixtures under pressures are not so many. Especially, as mentioned in the previous paper\(^1\), there are only a few investigations\(^2,3\) about the viscosity of nonpolar-polar mixtures under pressures. Therefore, as the example of the nonpolar-polar system, the viscosity of hydrogen-ammonia mixtures has been measured using a precision oscillating disk-type viscometer following the nitrogen-ammonia system\(^1\). In order to study the effect of the molecular weight of nonpolar gas on the viscosity of

\(^{*}\) Received March 31, 1978

* Presented in part at The 15th High Pressure Conference, Sapporo, Oct. 1st, 1976

1) M. Hongo and H. Iwasaki, This Journal, 47, 90 (1977)
2) H. Iwasaki and J. Kestin, Physica, 29, 1345 (1963)
polar gas, hydrogen was selected because its molecular weight is the smallest among nonpolar gases.

Measurements of the viscosity have been carried out at temperatures, 25, 50, 75 and 100°C and at pressures up to about $120 \times 10^5$ Pa for hydrogen and up to around the saturated vapor pressure of ammonia for hydrogen-ammonia mixtures, i.e., about $10 \times 10^5$ Pa at 25°C, $20 \times 10^5$ Pa at 50°C, $35 \times 10^5$ Pa at 75°C and $60 \times 10^5$ Pa at 100°C. The viscosity of the hydrogen-ammonia system at atmospheric pressure was measured by Trautz et al.4) (20 to 250°C) using a capillary-flow viscometer and by Pal et al.5) (33 to 260°C) using an oscillating disk viscometer, but there are no other viscosity data of this system to be compared with above atmospheric pressure.

**Experimental Method**

The apparatus and the experimental procedure are much the same as those reported in detail previously. But thermistor thermometers were used instead of thermocouples to measure the temperatures of the pressure vessel and the oil in the thermostat. These thermistor thermometers were calibrated against a platinum resistance thermometer provided with a calibration certificate by the National Bureau of Standards. The accuracies of the temperature measurements were ±0.01°C from 25 to 75°C and ±0.02°C at 100°C.

Hydrogen was supplied from the Nippon Oxygen Co., Ltd. and its purity was 99.99%. Ammonia was purified as described previously.

**Calculation of Viscosity**

The viscosity of the gases has been calculated in the same way as described in Ref. 2. The apparatus constant, $C_n'$, was determined using nitrogen at the temperature of 25°C and at pressures below $25 \times 10^5$ Pa. The mean value of $C_n'$ used in the present calculation was 1.1337 for hydrogen from 25 to 75°C, and 1.1355 for hydrogen at 100°C and for hydrogen-ammonia mixtures from 25 to 100°C.

The densities required for the calculation were obtained from the $PV$ values reported by Michels et al.6) for hydrogen and from $V_i$ chart prepared by K. Tezuka7) for hydrogen-ammonia mixtures, where $V_i$ is the ideal reduced molar volume. The accuracy of the experimental values of viscosity was estimated to be within ±0.3%.

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6) A. Michels and M. Goudeket, *Physica*, 8, 347 (1941)
Viscosity of Hydrogen and of Hydrogen-Ammonia Mixtures under Pressures

Results

The experimental results obtained for hydrogen are given in Table 1 and plotted in Fig. 1. The viscosity of hydrogen at the same experimental conditions as those of this work were already measured by Michels et al. 8) (25 to 75°C), Barua et al. 9) (25 to 75°C), and Gracki et al. 10) (25°C). They are also shown in Fig. 1. The values obtained in this work agree well with those obtained in the investigations described above within the experimental error. The experimental data given in Table 1 show that the initial slopes of the viscosity vs. pressure curves are slightly negative at 25, 50 and 75°C, although this behavior cannot be seen clearly in Fig. 1. Similar observations were pointed out by Chuang et al. 11) and others 9, 10), but the decrement ratio was smaller than the experimental accuracy.

The viscosity values obtained for hydrogen-ammonia mixtures are shown in Table 2. For example, the results obtained for mixtures at 25°C are shown in Fig. 2. The viscosity values for pure ammonia have already been reported in Ref. 1. It is apparent that the initial slope of the viscosity vs. pressure curves of each mixture, i.e., \( \frac{\partial \eta}{\partial P} \big|_{P=0} \), increases as the mole fraction of hydrogen increases, where \( \gamma \) is the viscosity of gases and \( P \) is the pressure. Fig. 3 shows the isobaric

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behavior of the viscosity of the hydrogen-ammonia system at 100°C. These curves show that the influence of pressure on the viscosity is not so large below the saturated vapor pressure of ammonia at the experimental conditions. All isobars obtained in the present measurements have the maximum at about 0.6 mole fraction of hydrogen.

The viscosity values of mixtures at atmospheric pressure were obtained by extrapolating the viscosity vs. pressure curves to 1 atm ($1.013 \times 10^5$ Pa), and are shown in Fig. 4 along with the data reported by Trautz et al.\textsuperscript{4} (20 and 100°C) and by Pal et al.\textsuperscript{5} (33, 54 and 98°C). The values obtained by Trautz et al.\textsuperscript{4} agree with those obtained in this work within ±1% at 100°C. However, the values obtained by Pal et al.\textsuperscript{5} are fairly different from those obtained in this work, although the experimental temperatures are not the same.
The viscosity of dilute gaseous binary mixtures can be evaluated by the method based on the kinetic theory\(^1\). The theoretical equation to the first approximation derived by Chapman and Enskog

is expressed by Eq. (8.2-22) in Ref. 12. In the calculation using the above equation, it is necessary to know the force constants between unlike molecules. The combination rules for nonpolar-polar interactions are represented as follows:

\[
\sigma_{np} = \frac{1}{2}(\sigma_n + \sigma_p) \xi^{-1/6} \tag{1}
\]

\[
\varepsilon_{np} = (\varepsilon_n \varepsilon_p)^{1/2} \xi^{1/2} \tag{2}
\]

where \(\sigma_n\) and \(\varepsilon_n\) are the Lennard-Jones potential parameters for the nonpolar molecules, \(\sigma_p\) and \(\varepsilon_p\) are the Stockmayer potential parameters for the polar molecules, and \(\xi\) is defined in Eq. (8.6-5) in Ref. 12. These parameters for pure gases in Eqs. (1) and (2) were calculated from Eq. (8.2-19) through third approximation in Ref. 12 for hydrogen and from Eq. (8.2-18) in Ref. 12 for ammonia\(^1\) using the experimental viscosity values of the gases at atmospheric pressure. The mean values are given as follows:

- \(\text{H}_2\): \(\sigma_n = 2.93_1\) [Å], \(\sigma_p = 3.15_1\) [Å], \(\varepsilon_n / k = 38.0\) [K]
- \(\text{NH}_3\): \(\sigma_n = 3.15_2\) [Å], \(\varepsilon_p / k = 358\) [K], \(\delta = 0.7\)

For the calculation of \(\gamma_{\text{mix}}\), based on Eq. (8.2-22) in Ref. 12, the theoretical viscosity values of hydrogen \([\gamma_1]\) were determined from Eq. (8.2-19) \(k=3\) by use of its potential parameters presented above and those of ammonia \([\gamma_2]\) were similarly done from Eq. (8.2-18) at each temperature.

Fig. 5 shows the comparison of the theoretical values based on Chapman-Enskog's theory (dashed line) with the experimental values (solid line). It may be seen from this figure that the experimental values obtained in this work are higher than the theoretical ones, and that the difference increases in the hydrogen-rich region as temperature rises up and it becomes about 3% at
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100°C.

In this study, it has been tried to modify the combination rule, Eqs. (1) and (2), using critical constants to fit to the experimental viscosity values, since there were some empirical methods\textsuperscript{13,14} to obtain the potential parameter by use of critical constants. It was found that the calculated values agreed well with the experimental values, when \( \varepsilon_{np} \) was somewhat decreased. So, the critical compressibility factor, \( Z_e \), was adopted to set up a correction factor, as it was known\textsuperscript{15} that a modification using \( Z_e \) expressed satisfactory results. \( Z_e \) of most substances have nearly constant values 0.24–0.31. The following equation was chosen, as a result of testing various formulae using \( Z_e \).

\[
\left( \frac{\varepsilon_{np}}{k} \right)^* = \frac{\varepsilon_{np}}{k} \left( \frac{(Z_{en})^{1/2} + (Z_{ep})^{1/2}}{} \right)^{-2}
\]

where \( Z_{en} \) and \( Z_{ep} \) are critical compressibility factors of nonpolar and polar substances, respectively. The viscosity values of \([\varphi_{mix}]\), obtained by applying Eq. (3), shown by dotted lines in Fig. 5, are in good agreement with the experimental ones.

The above-described method was also applied to the nitrogen-ammonia system\textsuperscript{12}, and the results are shown in Fig. 6. The force constants used for the nitrogen-ammonia system were obtained as follows:

\[
N_2: \ \varphi_{en}=3.732 \text{ [Å]}, \ \varepsilon_{en}/k=79.8 \text{ [K]}
\]

As can be seen from Figs. 5 and 6, the viscosity values obtained by using Eq. (3) agree very closely with the experimental ones from 25 to 75°C, but do not agree sufficiently at 100°C.

\textsuperscript{14} L. I. Stiel and G. Thodos, AIChE Journal, 10, 766 (1964)
\textsuperscript{15} T. Makita, “Viscosity and Thermal Conductivity”, Baifukan, Tokyo (1975)
Initial density dependence of the viscosity for the nonpolar-polar system

The gas viscosity \( \eta \) can be approximately expressed as a function of the density \( \rho \) as follows:

\[
\eta = \eta_0 (1 + \alpha' \rho + \cdots)
\]

where \( \eta_0 \) is the viscosity extrapolated to zero density and \( \alpha' = \gamma^{-1} (\partial \eta / \partial \rho)_{\rho=0} \) is the initial density dependence of viscosity\(^{1)}\). In this work the experimental viscosities of hydrogen and hydrogen-ammonia mixtures were expressed by the cubic equation as

\[
\eta = \eta_0 (1 + \alpha' \rho + \beta' \rho^2 + \gamma' \rho^3)
\]

and the constants in Eq. (5) were determined by means of the least-squares method as given in Table 3. The relation between \( \alpha' \) and \( x_{\text{H}_2} \), at each temperature is shown in Fig. 7, where \( \alpha' \) denotes the initial density dependence of the viscosities of ammonia\(^{1)}\) and of hydrogen-ammonia mixtures, and \( x_{\text{H}_2} \), the mole fraction of hydrogen. As shown in the figure, each isotherm is approximated by a straight line, and then it is found in the nitrogen-ammonia system\(^{1)}\) that \( \alpha' \) increases with an increase in temperature and in the mole fraction of hydrogen and that \( x_{\text{H}_2} \), the mole fraction of hydrogen at a point of intersection of each straight line with \( \alpha'=0 \), decreases with an increase in temperature. Fig. 8 shows that there is the linear relation between \( x_{\text{H}_2} \) and temperature. It should be noted that the similar relation was observed in case of the nitrogen-ammonia system\(^{1)}\) as shown in Fig. 8. It is obvious that two straight lines are parallel to each other.

### Table 3

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<th>( \eta_0 )</th>
<th>( \alpha' )</th>
<th>( \beta' )</th>
<th>( \gamma' \cdot 10^{-3} )</th>
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a) \( \eta = \eta_0 (1 + \alpha' \rho + \beta' \rho^2 + \gamma' \rho^3) \)

\( \eta : 10^{-7} \) Pa·s  \( \rho : 10^3 \) kg·m\(^{-3}\) = g·cm\(^{-3}\)
The viscosity of polar gases, such as ammonia, sulfur dioxide, water vapor etc., decreases with an increase in pressure below a certain temperature. It was considered by Stogryn and Hirschfelder\(^{16}\) that the gas was a mixture of monomers and dimers, and that the initial pressure dependence of viscosity depended on a dimerization effect and a collisional transfer effect. As described in Ref. 1, it can be presumed that polar molecules, such as ammonia, sulfur dioxide etc. form dimers, by considering that water molecules are possible to form dimers\(^{17}\). Then, \(\alpha'\) for the polar gases is more strongly influenced by the dimerization of their molecules than that for nonpolar gases. Fig. 7 seems to suggest\(^{15}\) that the rise of temperature and the presence of nonpolar molecules disturb the dimer formation of polar molecules. In addition, from Fig. 8 it may be concluded in these two systems that the nonpolar molecules of larger molecular weight disturb more strongly the dimerization of polar molecules than those of smaller molecular weight.

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\begin{itemize}
  \item \(^{16}\) D. E. Stogryn and J. O. Hirschfelder, \textit{J. Chem. Phys.}, \textbf{31}, 1545 (1959)
  \item \(^{17}\) J. P. O'Connel and J. M. Prausnitz \textit{IEC Fundamentals}, \textbf{8}, 453 (1969)
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