Pressure Dependence of Viscosity of Polar Gases

By

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Viscosity of polar gases, such as steam and ammonia, decreases with increasing pressure. In order to explain this anomaly, we considered a polar gas to be a mixture of dimers and monomers. The viscosity of steam and ammonia was calculated as the sum of mixture term η_{mix} and collisional transfer term η_c, namely $\eta = \eta_{mix} + \eta_c$. The calculated and experimental values of viscosity of these gases agreed qualitatively well, and the negative pressure dependence of viscosity of these gases was explained with reasonable success by the theory of association.

Introduction

For the transport properties of dilute gases Chapman and Enskog developed a very complete theory. Their rigorious development is based on knowledge of the distribution function that satisfies the Boltzmann integro-differential equation. The theory of Chapman and Enskog has the following restrictions; only binary collisions are considered, so that the results do not apply at densities where three-body collisions become important; all collisions are elastic, and pairs of molecules interact according to a single central force law so that the force depends only on the distance of separation between the molecules. Thus the Chapman-Enskog theory can apply strictly only at low pressures and only to the noble gases.

When we wish to extend the theory for polar gases, we must consider the effects of orientation -dependent forces and inelastic collisions. Krieger, Itean et al. and Monchick and Mason overcame the complications due to orientation-dependent forces by introducing several assumptions, by which the problem of orientation-dependent forces is changed from difficult collision dynamics to easier kinetic theory.

In dilute gas theory, it is assumed that there are two-body collisions only and that the molecules have no finite extention in space. In dense gases, however, these

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two assumptions are not valid. Enskog was the first to make an advance in this direction, by developing a kinetic theory of dense gases made up of rigid spherical molecules. For this special model there are essentially no three body and higher order collisions. By considering only two-body collisions he was able to develope a theory of dense gases. Enskog's theory turned to be applicable to real gases with reasonable success.   However, the theory considers *essentially* two body collisions only, and many attempts have been made to develope more rigorous theory of dense gases which tries to account not only for binary collisions but also triple collisions, quadruple collisions, etc. Such an approach was initiated by Bogoliubov and succeeded in by Hoffman and Curtiss, and Sengers, etc. At the present, however, the Enskog theory is still the only one that can be applied to gases at high density.

Another approach for calculating the initial pressure dependence of transport properties of dense gases is more promising for use at low temperatures. The initial pressure dependence of transport properties can be assumed to arise from molecular association, and in particular, a dense gas is assumed to be a mixture of monomers and dimers. The first treatment of this kind was done by Stogryn and Hirschfelder.

The viscosity of most gases increases with increasing pressure due to collisional transfer of momentum and can be accounted for approximately by Enskog theory of dense gases. However, the viscosity of some polar gases, such as steam and ammonia, decreases with increasing pressure.   Butane and helium also show initial decrease of viscosity with increase of pressure.

In this paper the authors calculate the viscosity of two polar gases, namely steam and ammonia by association theory, considering these gases to be mixtures of monomers and dimers.

Viscosity of Dilute Gas and Binary Mixture of Dilute Gases

As a polar gas is considered to be mixture of monomers and dimers at moderate pressures, it is necessary to know the equation for a mixture as well as the equation for a pure gas.   From Chapman and Enskog theory the viscosity of a pure gas is given by[1],[2]

$$\eta = 26.693 \frac{\sqrt{MT}}{\sigma^2 \, \Omega^{(2,2)*}(T^*)} \tag{1}$$

where η = viscosity in μP

T = temperature in °K

T^* = reduced temperature = kT/ε

M = molecular weight

σ = collision parameter in Å

ϵ/k = potential parameter in °K

$\Omega^{(2,2)}(T^*)$ = collision integral defined in (7)

In order to obtain the viscosity of a binary mixture it is convenient to define a quantity η_{12} thus:

$$\eta_{12} = 26.693 \frac{\sqrt{2M_1 M_2 \, T/(M_1 + M_2)}}{\sigma_{12}^2 \, \Omega_{12}^{(2,2)*}(T_{12}^*)} \qquad (2)$$

where $\quad T_{12}^* = kT/\epsilon_{12}$ = reduced temperature

M_1, M_2 = molecular weights of species 1 and 2

$\sigma_{12}, \epsilon_{12}/k$ = parameters in the potential functions characteristic, of 1–2 interaction (in Å and °K respectively)

We may write the viscosity of a binary mixture in terms of the quantities defined in (1) and (2):

$$\frac{1}{\eta_{mix}} = \frac{X_\eta + Y_\eta}{1 + Z_\eta} \qquad (3)$$

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

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

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

where $\quad x_1, x_2$ = mole fractions of species 1 and 2

A_{12}^* = a function of kT/ϵ_{12} defined in (8)

In order to caluculate of $\Omega^{(2,2)*}$ and A_{12}^* for any potential function $\varphi(r)$, the angle of deflection in a collision $\varkappa$, must first be calculated according to the following equation:

$$\varkappa(b,g) = \pi - 2b \int_{r_m}^{\infty} \frac{dr/r^2}{\sqrt{1 - (\varphi(r)/\frac{1}{2}\mu g^2) - (b^2/r^2)}} \qquad (4)$$

In above equation, b is the distance of closest approach in the absence of the potential $\varphi(r)$; g is the relative speed of the colliding molecules; μ is reduced mass of the two colliding molecules; r_m is the distance of closest approach in the actual collision, or r_m is the largest value of r for which

$$1 - (2\,\varphi(r)/\mu g^2) - (b^2/r^2) = 0 \tag{5}$$

For rigid spherical molecules it is easy to write an analytical expression for x, but for any realistic potential function, numerical methods must be used. Finally the collision integrals are given,

$$\varOmega^{(l,s)}(T) = \sqrt{2\pi kT/\mu} \int_0^\infty e^{-\gamma^2} \gamma^{2s+3}(1 - \cos^l x)\, bdbd\,\gamma \tag{6}$$

where $\gamma^2 = \dfrac{1}{2}\,\mu g^2/kT$, and l and s are positive integers.

It is convenient to reduce $\varOmega^{(l,s)}(T)$ by dividing it by its corresponding rigid sphere value, thus

$$\varOmega^{(l,s)*}(T^*) = \frac{[\varOmega^{(l,s)}]}{[\varOmega^{(l,s)}]_{rig\ sph}}. \tag{7}$$

and $\quad A^* = \varOmega^{(2,2)*}/\varOmega^{(1,1)*} \tag{8}$

The interaction potential which has been used almost exclusively for polar gases is the Stockmayer potential,

$$\varphi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{D^2}{r^3}\,\zeta \tag{9}$$

where $\quad \zeta = 2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi \tag{10}$

and D is the dipole moment, θ_1 and θ_2 are the angles of inclination of the axes of the two dipoles to the line joining the centers of molecules, and ϕ is the azimuthal angle between them. When there is no dipole moment the equation (9) reduces to just the Lennard-Johns (12–6) potential with a potential well depth ϵ and a diameter σ for which $\varphi(r)=0$.

The equation (9) can be written in the following form,

$$\varphi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \delta\left(\frac{\sigma}{r}\right)^{3}\right] \tag{11}$$

where $\quad \delta = \dfrac{1}{4}D^{*2}\zeta, \quad D^* = D/(\epsilon\sigma^3)^{1/2} \tag{12}$

In the first attempt to treat polar gases, Krieger[3] assigned a fixed value of 2 to ζ. This corresponds to a model where the dipoles maintain a head-to-tail position, throughout the encounter. This approximation has the advantage that it replaces an angle-dependent force by a central force, and limits consideration to only one relative orientation. Although Krieger's results looked fairly reasonable, Itean,

Glueck, and Svehla[4] have detected an error in his calculations. When this was corrected, and the calculations repeated using the same model, the emprical values of σ and ϵ obtained by fitting the available experimental data were physically unrealistic.

Monchick and Mason[5] have approximated collision integrals by making the following two assumptions. They first assumed that the inelastic collisions, even if they occur frequently, have little effect on the trajectories. Their second assumption concerns the effect of orientation-dependent forces on the angle of deflection χ. They argue that although the orientation-dependent forces act along the whole trajectory, the angle of deflection is determined primarily by the interaction in the vicinity of the distance of closest approach. Over a small range near the distance of closest approach the relative orientation does not change much so that in each collision χ is determined largely by only one relative orientation. This is equivalent to replacing (11) with a multitude of spherically symmetrical potential corresponding to all values of ζ between -2 and $+2$. The collision integrals were then evaluated and averaged over all relative orientations.

This is the most reasonable theoretical model available for polar gases, and in this paper all values of collision integrals are taken from the tables of Monchick and Mason.

Viscosity of Dense Gases

The first work on the transport properties of dense gases was due to Enskog[1,2]. He developed the theory of dense gases made up of rigid spherical molecules by considering only two-body collisions and by taking into account the size of molecules. The frequency of collisions in a gas made up of rigid spheres differ by a factor Y from that in a gas made up of point particles. The equation of state for rigid spheres in terms of Y is

$$\frac{p\tilde{V}}{RT} = 1 + \frac{b_0}{\tilde{V}} Y \tag{13}$$

where $b_0 = \dfrac{2}{3} \pi \tilde{N} \sigma^3$ is the second virial coefficient of rigid spheres, $\tilde{V}$ is the volume per one mole and $\tilde{N}$ is the number of rigid spheres of one mole.

The quantity Y can be obtained as follows,

$$Y = 1 + 0.6250 \left(\frac{b_0}{\tilde{V}}\right) + 0.2869 \left(\frac{b_0}{\tilde{V}}\right)^2 + 0.115 \left(\frac{b_0}{\tilde{V}}\right)^3 + \cdots\cdots \tag{14}$$

in connection with the virial expansion of the equation of state of rigid spheres.

Enskog equation for viscosity derived is

$$\frac{\eta \tilde{V}}{\eta_0 b_0} = \frac{1}{y} + 0.8 + 0.761\, y \qquad (15)$$

where η_0 is the zero density viscosity and $y = (b_0/V)Y$.

For rigid spherical molecules the parameter y is equal to the compressibility factor minus one:

$$y = \left(\frac{p\tilde{V}}{RT}\right) - 1 \qquad (16)$$

In the region of low and moderate densities y may be written in the virial form:

$$y = \left(\frac{b_0}{\tilde{V}}\right) + 0.6250\left(\frac{b_0}{\tilde{V}}\right)^2 + 0.2869\left(\frac{b_0}{\tilde{V}}\right)^3 + 0.115\left(\frac{b_0}{\tilde{V}}\right)^4 + \cdots\cdots \qquad (17)$$

In order to apply the equation (15) to real gases Enskog suggested that the pressure in the equation (16) be replaced by the thermal pressure $T(\partial p/\partial T)_{\tilde{v}}$, so that y may be determined from the experimental $p - \tilde{V} - T$ data by using the relation,

$$y = \frac{\tilde{V}}{RT}\left[T\left(\frac{\partial p}{\partial T}\right)_{\tilde{v}}\right] - 1 = \frac{B}{\tilde{V}} + \frac{C}{\tilde{V}^2} + \cdots\cdots \qquad (18)$$

where B, C, etc., are the virial coefficients.

In real gases the values of b_0 can not be assigned arbitrarily nor calculated from the relation $b_0 = \frac{2}{3}\pi \tilde{N}\sigma^3$. In order that η_0 be the zero density viscosity, it is necessary that $y\tilde{V} \to b_0$ as $\tilde{V} \to \infty$, namely the density tends to zero. From the equation (18), it follows that

$$b_0 = B + T\frac{dB}{dT} \qquad (19)$$

Viscosity of Polar Gases at Moderate Pressures

The viscosity of polar gases at moderate pressures is given by,

$$\eta = \eta_{mix} + \eta_c \qquad (20)$$

where the term η_{mix} is due to molecular association, and the term η_c is due to collisional transfer. When considering the initial pressure dependence, only the

dimerization reaction for association

$$2A \rightleftharpoons A_2 \tag{21}$$

need be taken into account. Then η_{mix} is the coefficient of viscosity for a binary mixture of monomers and dimers predicted by the Chapman-Enskog theory.

The equation of state of an imperfect gas may be written,

$$p\,(V - b_a) = (n_1 + n_2)\,RT \tag{22}$$

where n_1 is the number of moles of monomers and n_2 is the number of moles of dimers, and b_a is excluded volume. The numbers of monomers and dimers are determined by an ordinary equlibrium constant for association,

$$K\,(T) = n_2\,V/n_1{}^2 \tag{23}$$

$$K\,(T) = x_2\,\tilde{V}/x_1{}^2 = \frac{x_2}{(1 - x_2)^2}\,\tilde{V} \tag{24}$$

In the limit that V is very large n_1 approaches unity and n_2 approaches the value $K(T)/V$. Rearranging the equation of state (22) into the virial form, it is evident that

$$B\,(T) = b_a - K\,(T) \tag{25}$$

Collisional transfer term η_c is obtained by expanding Enskog equation (15) with the relation (17) in powers of $b_0/\tilde{V}$. If we neglect higher terms than $(b_0/\tilde{V})^2$, the result is

$$\eta_c = \frac{7}{40} \left[B + T\left(\frac{dB}{dT}\right) \right] \frac{\eta_0}{\tilde{V}} \tag{26}$$

Comparison of Theory and Experiment of Viscosity of Polar Gases

In order to apply the Chapman and Enskog equation (3) for a mixture of monomers and dimers, it is necessary to know the relations between the parameters on Stockmayer potential. Stogryn and Hirschfelder[6] calculated with regard to ϵ_{ij} and σ_{ij},

$$\epsilon_{12}/\epsilon_{11} = 1.32 \tag{27}$$

$$\sigma_{12}/\sigma_{11} = 1.16 \tag{28}$$

For the maximum value of the dipole moment contribution term δ_{max}, Barua and Das Gupta[7] gave the results, $(\delta_{max})_{12} = 1.44$ for steam of which $(\delta_{max})_{11} = 1.2$,

and $(\delta_{max})_{12}=0.85$ for ammonia of which $(\delta_{max})_{11}=0.7$. Force constants for dimers, ϵ_{22}, σ_{22} and $(\delta_{max})_{22}$ can be obtained by the empirical combination rules[8],

$$\epsilon_{22} = \epsilon_{12}^2/\epsilon_{11} \tag{29}$$

$$\sigma_{22} = 2\sigma_{12} - \sigma_{11} \tag{30}$$

$$(\delta_{max})_{22} = \frac{(\delta_{max})_{12}}{(\delta_{max})_{11}} \cdot \frac{\sigma_{12}^6}{(\sigma_{11} \cdot \sigma_{22})^3} \tag{31}$$

With above relations the force constants for steam and ammonia obtained are given in Table 1.

Table 1. Parameters for steam and ammonia

	ϵ_{11}/k (°K)	ϵ_{12}/k (°K)	ϵ_{22}/k (°K)	δ_{11} (Å)	δ_{12} (Å)	δ_{22} (Å)	$(\delta_{max})_{11}$	$(\delta_{max})_{12}$	$(\delta_{max})_{22}$
Steam	506	668	882	2.71	3.15	3.59	1.2	1.44	1.83
Ammonia	358	473	624	3.15	3.65	4.16	0.7	0.85	1.09

The values of excluded volume adapted are $b_a=38.5$ $cm^3/mole$ for steam and $b_a=62.8$ $cm^3/mole$ for ammonia respectively[9]. The second virial coefficients of steam[10] and ammonia[11] are given respectively as,

$$\frac{B(T)}{\left[\frac{cm^3}{mole}\right]} = 461.51 \times 18.016 \times \left(\frac{T}{100}\right)^{-5} \times \left\{-1.57757 \times 10^2\right.$$

$$+ 7.9566 \times 10 \times \left(\frac{T}{100}\right) - 1.52099 \times 10 \times \left(\frac{T}{100}\right)^2$$

$$\left.+ 6.11042 \times 10^{-1} \times \left(\frac{T}{100}\right)^3\right\} \tag{32}$$

$$\frac{B(T)}{\left[\frac{cm^3}{mole}\right]} = 20.8 - \frac{2.05}{T^2} \times 10^7 \tag{33}$$

The volumes per mole for steam and ammonia are calculated by the equations of state given in the Appendix.

With the values of b_a, $B(T)$ and $\tilde{V}$, the mole fraction of dimers x_2 is directly calculated by the equation (24). In applying the equation (3) for steam and ammonia, all values $\Omega^{(2,2)*}$ and A^* were taken from the Monchick and Mason's tables on Stockmayer potential.

The collisional transfer term η_c for steam and ammonia was calculated from the equation (26) with the second virial coefficient equations (32) for steam and

(33) for ammonia respectively.

Table 2. Calculated and experimental values of the viscosity of steam

t (°C)	p (atm)	x_2	η_{mix} (μP)	η_{cal} (μP)	η_{expt} (μP)	η_{Barua} (μP)
175	4.09	0.030	151.94	153.58	150.7	
175	8.29	0.059	147.93	151.36	148.6	
200	7.36	0.043	158.89	161.20	159.1	
200	10.23	0.059	156.59	159.87	158.0	
200	12.14	0.070	155.12	159.06	157.4	
200	13.75	0.078	153.91	158.43	156.3	
225	6.23	0.031	169.81	171.36	170.3	
225	10.17	0.049	166.92	169.51	168.6	
225	15.44	0.073	163.33	167.36	168.1	
225	20.23	0.095	160.26	165.70	166.3	
250	9.73	0.041	176.95	178.98	180.6	
250	14.69	0.060	173.88	177.00	180.2	
250	19.27	0.077	171.20	175.37	179.4	
250	24.38	0.096	168.36	173.78	178.2	
250	28.73	0.112	166.05	172.58	177.6	
275	12.04	0.043	185.21	187.35	190.8	
275	24.28	0.083	178.71	183.21	189.7	
275	34.09	0.114	174.02	180.60	187.7	
275	43.62	0.143	169.77	178.58	185.9	
300	6.06	0.019	198.36	199.28	203.5	
300	12.08	0.038	195.07	196.93	202.9	
300	19.67	0.060	191.22	194.31	201.7	
300	27.27	0.081	187.65	192.03	200.6	
300	35.92	0.105	183.86	189.80	199.3	
300	43.86	0.126	180.60	188.06	198.2	
350	10.0	0.025	215.81	217.01		222.1
350	30.0	0.070	207.30	211.05		223.0
350	50.0	0.111	200.02	206.54		225.5
350	70.0	0.149	193.58	203.19		229.2
400	10.0	0.020	234.60	235.60		
400	30.0	0.057	227.08	230.18		
400	50.0	0.090	220.52	225.84		
400	70.0	0.122	214.69	222.39		

In Table 2 the calculated values of viscosity of steam are shown with the ex-
perimental values of Rivkin and et al. and also the calculated values due to Barua
and Das Gupta. The negative pressure dependence of viscosity of steam was first
shown experimentally by Kestin et al.[12),13)], and has been comfirmed by Rivkin et

al.[14],[15] and Sato et al.[16] These three sets of data agree very well. As the data of Rivkin et al. are the most comprehensive, only their experimental values are listed in Table 2. In Fig. 1 a comparison of the calculated and experimental values of the viscosity of steam is given. Some of the experimental results due to Kestin et al. and Sato et al. are also shown in this figure. The calculated and experimental results agree quite satisfactorily under about 250 °C, Above 250 °C. however, departure of the calculated values from the experimental results increases with increasing temperature.
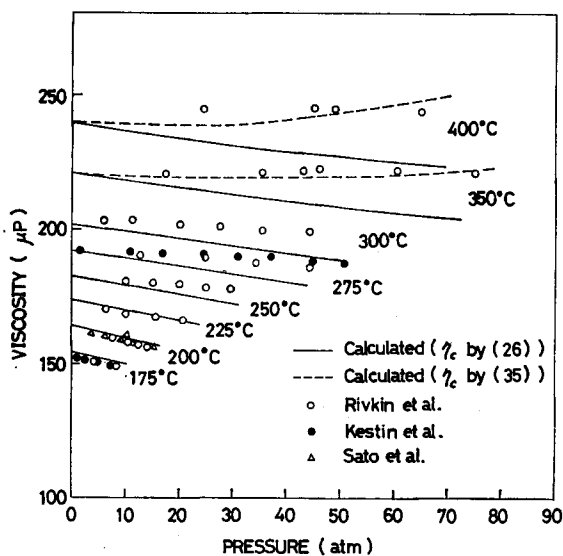

Fig. 1. A comparison of calculated and experimental viscosities of steam

Although the results of Barua et al. seem to be reasonable, we are sure there is an error in their calculation of the derivative of second virial coefficient, that is dB/dT. In order to prove this, we also calculated the viscosity of steam with another equation of the second virial coefficient[17],

$$\frac{B(T)}{\left[\frac{cm^3}{mole}\right]} = 18.016 \times \left\{1.8529 - 30.676 \times \left(\frac{T}{100}\right)^{-1} - 127.43 \times \left(\frac{T}{100}\right)^{-2}\right.$$

$$\left. - 1298.81 \times \left(\frac{T}{100}\right)^{-3}\right\} \tag{34}$$

and found no appreciable difference from the results of the equation (32).

The departure of the calculated results from the experimental results at higher temperatures may be mainly attributed to inappropriatness of the equation (26)

for collisional transfer term η_c, since it is derived from the equation for rigid spherical molecules. Then we calculated this term by using the original Enskog equation (15) as,

$$\eta_c = \eta_0 \left\{ \frac{b_0}{\tilde{V}} \left(\frac{1}{y} + 0.8 + 0.761\,y \right) - 1 \right\} \tag{35}$$

The results are also shown in Fig. 1. At higher temperatures, namely 350 °C and 400 °C, these values seem to give better results. Unfortunately this term becomes negative at lower temperatures under about 300 °C. Taking into account the very complicated behavior of properties of steam, it seems natural that Enskog equation is applicable to a limited temperature range.

In Table 3 and Fig. 2 the calculated and experimental results of viscosity of ammonia are shown as in the case of steam. The experimental results are due to Iwasaki et al.[18] and Carmichael et al.[19] Considering the inconsistency of these two sets of data, the qualitative agreement of calculated and experimental results is

Table 3. Calculated and experimental values of the viscosity of ammonia

| t (°C)	p (atm)	x_2	η_{mix} (μP)	η_{cal} (μP)	η_{expt} (μP)
20.0	1.10	0.013	99.37	99.57	98.82
20.0	1.53	0.018	98.99	99.28	98.65
20.0	2.03	0.023	98.56	98.94	98.47
20.0	3.04	0.034	97.71	98.29	98.08
20.0	4.06	0.045	96.87	97.67	97.74
20.0	5.04	0.056	96.10	97.10	97.34
20.0	6.04	0.066	95.33	96.55	96.95
30.0	1.04	0.011	102.87	103.05	102.80
30.0	1.11	0.012	102.81	103.01	102.71
30.0	1.53	0.016	102.46	102.73	102.56
30.0	1.99	0.021	102.08	102.44	102.44
30.0	3.01	0.031	101.27	101.81	102.13
30.0	3.75	0.038	100.69	101.38	101.90
30.0	4.99	0.050	99.76	100.69	101.48
30.0	5.69	0.057	99.24	100.31	101.27
30.0	6.18	0.062	98.89	100.06	101.15
37.8	1.16	0.011	105.56	105.76	106.54 [a]
37.8	11.73	0.106	98.22	100.47	104.28 [a]
71.1	1.76	0.013	116.90	117.16	118.87 [a]
71.1	11.90	0.082	111.00	112.84	118.19 [a]

[a] These are the averaged values.
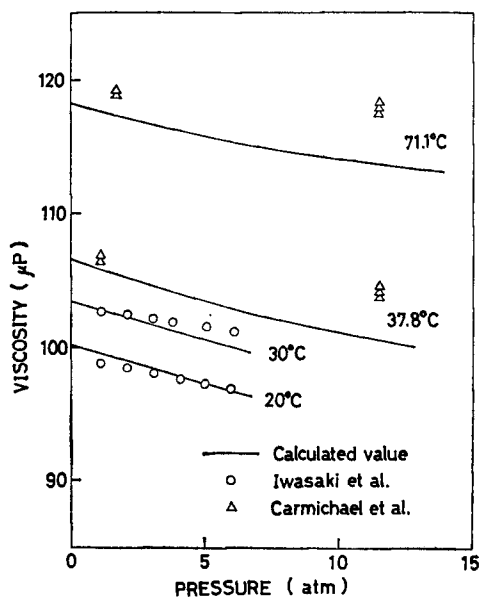
Fig. 2. A comparison of calculated and experimental viscosities of ammonia

fairly good. For the calculation of collisional transfer term η_c the equation (35) was also tried to be applied, but in this case this term turned out to be negative at all temperatures under consideration, and the results are not shown here.

Conclusion

Viscosity of two polar gases, namely steam and ammonia, was calculated as the sum of the term due to molecular association, and the term due to collisional transfer. The calculated results have well reproduced the negative pressure gradient of these polar gases. The qualitative agreement of calculated and experimental results seems fairly good, taking into account the empirical nature of the combination rules and the equilibrium constant for association.

References

1) S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge University Press, New York, 1952), 2nd ed.
2) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954).
3) F. J. Krieger, Project Rand Research Memorandum No. RM-646 (July, 1951).
4) E. C. Itean, A. R. Glueck, and R. A. Svehla, NASA Technical Note D-481 (January, 1961).
5) L. Monchick and E. A. Mason, J. Chem. Phys., 35 1676 (1961)
6) D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys., 31 1545 (1959)

7) A. K. Barua and A. Das Gupta, Trans. Faraday Soc., **59** 2243 (1963)
8) E. A. Mason and L. Monchick, J. Chem. Phys., **36** 2746 (1962)
9) J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, J. Chem. Phys., **10** 201 (1940)
10) T. Sato, T. Minamiyama, and J. Yata, Memoirs of Faculty of Engineering, Kyoto University, **29** Part 1 p 1. (1967)
11) P. Davies in Thermodynamic Functions of Gases, edited by F. Din (Butterworth's Scientific Publications Ltd., London, 1956), Vol. 1, p 33
12) J. Kestin and H. Wang, Physica, **26** 575 (1960)
13) J. Kestin and P. D. Richardson, Brown University, (June, 1962)
14) S. L. Rivkin and A. S. Levin, Teploenergetika, No. 4 (1966)
15) S. L. Rivkin, A. S. Levin, and L. B. Israilevsky, 7th International Conference on the Properties of Steam, Tokyo, (1968)
16) T. Sato et al., Preprint of the annual meeting of JSME, No. 704-4 p 7 (1970)
17) S. Sugawara, T. Sato, T. Minamiyama, and J. Yata, JSCP Report No. 11 (1963)
18) H. Iwasaki, J. Kestin, and A. Nagashima, J. Chem. Phys., **40** 2988 (1964)
19) L. T. Carmichael, H. H. Reamer, and B. H. Sage, J. Chem. Eng. Data, **8** 400 (1963)

Appendix

[1] The equation of state for steam used for evaluation of specific volume is as follows;

$$v = \frac{RT}{p}(1 + B_1 p + C_1 p^2 + D_1 p^3 + E_1 p^4 + F_1 p^5 + G_1 p^{10}) \qquad (A1)$$

where

$$B_1 = \left(\frac{T}{100}\right)^{-6} \sum_{i=0}^{3} b_i \left(\frac{T}{100}\right)^i, \qquad C_1 = \left(\frac{T}{100}\right)^{-8} \sum_{i=0}^{3} c_i \left(\frac{T}{100}\right)^i$$

$$D_1 = \left(\frac{T}{100}\right)^{-14} \sum_{i=0}^{3} d_i \left(\frac{T}{100}\right)^i, \qquad E_1 = \left(\frac{T}{100}\right)^{-18} \sum_{i=0}^{4} e_i \left(\frac{T}{100}\right)^i$$

$$F_1 = \left(\frac{T}{100}\right)^{-24} \sum_{i=0}^{9} f_i \left(\frac{T}{100}\right)^i, \qquad G_1 = \left(\frac{T}{100}\right)^{-60} \sum_{i=0}^{8} g_i \left(\frac{T}{100}\right)^i$$

$$R = 4.6151 \quad cm^3 \cdot bar/°K$$

$$p = \text{pressure in bar}$$

The coefficients b_i, c_i, d_i, e_i, f_i, and g_i are given in the table below.

$$
\begin{array}{lll}
b_0 = -1.57757\times10^2 & e_0 = -4.962341\times10^6 & f_7 = 1.1520755660\times10^7 \\
b_1 = 7.95660\times10 & e_1 = 2.7268359\times10^6 & f_8 = -3.7879899122\times10^5 \\
b_2 = -1.52099\times10 & e_2 = -5.5614552\times10^5 & f_9 = 5.4896910962\times10^3 \\
b_3 = 6.11042\times10^{-1} & e_3 = 4.9619002\times10^4 & g_0 = -2.0213590577\times10^{29} \\
c_0 = -6.66136\times10 & e_4 = -1.6246985\times10^3 & g_1 = 2.4391506627\times10^{29} \\
c_1 = 2.54163\times10 & f_0 = -3.6578825095\times10^{11} & g_2 = -1.2786060893\times10^{29} \\
c_2 = -3.54131 & f_1 = 4.6173978134\times10^{11} & g_3 = 3.8016907475\times10^{28} \\
c_3 = 1.699274\times10^{-1} & f_2 = -2.5646414340\times10^{11} & g_4 = -7.0099067456\times10^{27} \\
d_0 = -5.63782\times10^4 & f_3 = 8.2302553144\times10^{10} & g_5 = 8.2048713917\times10^{26} \\
d_1 = 2.26637\times10^4 & f_4 = -1.6822078787\times10^{10} & g_6 = -5.9510031176\times10^{25} \\
d_2 = -3.16215\times10^3 & f_5 = 2.2714415302\times10^9 & g_7 = 2.4445612987\times10^{24} \\
d_3 = 1.48170\times10^2 & f_6 = -2.0264849375\times10^8 & g_8 = -4.3530858263\times10^{22}
\end{array}
$$

The thermal pressure derived from the equation (A1) is,

$$
T\left(\frac{\partial p}{\partial T}\right)_v = \frac{1/p + \left(T+\frac{dB_1}{dT}\right) + \left(T+\frac{dC_1}{dT}\right)p + \left(T+\frac{dD_1}{dT}\right)p^2 +}{1/p^2 - C_1 - 2D_1 p - 3E_1 p^2 - 4F_1 p^3}
$$

$$
\frac{\left(T+\frac{dE_1}{dT}\right)p^3 + \left(T+\frac{dF_1}{dT}\right)p^4 + \left(T+\frac{dG_1}{dT}\right)p^9}{-9G_1 p^8}
$$

(A2)

[II]   The equation of state used for ammonia is,

$$
\frac{v}{\left[\dfrac{cm^3}{mole}\right]} = \frac{82.0697}{p} - \frac{58.017\times10^8}{T^3}
$$

$$
- \frac{(0.062904+0.055898\cdot p)\times10^{29}}{T^{11}} - \frac{0.121205\cdot p^5\times10^{43}}{T^{19}}
$$

$$
+ 10^{-3}\times(97.5906 - 6.9228\cdot p + 0.465099\cdot p^2 - 0.011416\cdot p^3
$$

$$
+ 0.000134\cdot p^4)\,T - 43.056 - 0.6335\,p \tag{A3}
$$

where p = pressure in atomosphere