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Measurement of Viscosities of Gases at High Pressure. II

Viscosities of Nitrogen and Mixtures of Nitrogen and Hydrogen

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Synopsis

Measurements of the viscosities of nitrogen, 80.4% N₂—19.6% H₂ system and 31.9% N₂—68.1% H₂ system have been made within the error of about 1 per cent, using the modified oscillating disc method, at the following conditions:

namely,

pure nitrogen at 25°, 100° and 150°C up to 200 atm,
80.4% N₂—19.6% H₂ system at 50° and 100°C up to 200 atm,

and

31.9% N₂—68.1% H₂ system at 50°C up to 200 atm and
at 100°C up to 100 atm.

From these measurements it was found that $(\partial\eta/\partial\theta)_p$ is positive while $(\partial\eta/\partial p)_\theta$ becomes progressively smaller as the temperature increases and that $(\partial\eta/\partial\theta)_p$ is positive, remains constant over the whole density ranges within the limits of the experimental accuracy and is the function of the temperature alone.

The experimental equations for viscosity-density isotherms were derived using the measured values. These equations reproduce them within the experimental accuracy.

Calculating from the measured values, it was found that the deviations $(\Delta_{(\eta)})$ of the viscosities of binary mixtures (η_m) from those $(n_N\eta_N + n_H\eta_H)$ made equal to the molal average of the viscosities of the components of the mixture are independent of the pressure within the experimental accuracy over the whole measured ranges and are the function of the temperature and the concentration ratio of components.

I. Introduction

Measurements have recently been made by a number of observers^{*)} on the viscosities of pure gases at high pressures. From a theoretical point of view also, Enskog *et al*⁽¹⁾ have developed the viscosity equations, and there are not a few⁽²⁾ who have investigated the applicability of his equation by measured values. Besides, much attention⁽³⁾ has been paid on how to predict the results. However, it is very difficult to study binary mixtures theoretically at high pressures, and so few measurements have been made of gases, except of air.*) Measured values

*) *cf.* literature cited in 6).

- (1) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases" (Camb. Univ. Press, 1952); M. Born and H. S. Green, Proc. Roy. Soc., A **190** (1947), 455; L. M. Yang, Nature, **161** (1948), 523; and others.
- (2) A. Michels and R. O. Gibson, Proc. Roy. Soc., A **134** (1931), 288; O. I. Leipunskii, Acta. physicochimica U. R. S. S., **18** (1943), 172, C. A., **38** (1944), 4484; E. W. Comings and M. F. Nathan, Ind. Eng. Chem., **39** (1947), 964; E. Kuss, Z. angew. Physik, **4** (1952), 203; and others.
- (3) O. A. Uyehara and K. M. Watson, Natl. Petroleum News, **36** (1944), R 764; E. W. Comings and R. S. Egly, Ind. Eng. Chem., **32** (1940), 714; and others.

obtained by Boyd⁽⁴⁾ at 30° and 70°C up to 200 atmospheres on 64.1% H₂—35.9% N₂ system are nothing but qualitative, judging from the accuracy of measurement *et al*; after all, we may safely conclude that there have scarcely been any measured values for us to discuss the viscosities of mixtures at high pressures.

While in the industrial field, many deal with mixtures at high pressures. At that time, considering pseudo-critical constants, they deal with them just as they do with a pure gas, and apply the old methods of prediction on it to them and analogize the values.⁽⁵⁾ But it is necessary to obtain accurate viscosity values in order to know the reliability of such a method, and to get a more accurate method of prediction.

This paper continues from the preceding one.⁽⁶⁾ As a set of binary mixtures, nitrogen and hydrogen were chosen; measurements were made of pure nitrogen at 25°, 100° and 150°C up to 200 atmospheres, of 81.4% N₂—19.6% H₂ system, at 50° and 100°C up to 200 atmospheres, and of 31.9% N₂—68.1% H₂ system, at 50°C up to 200 atmospheres, at 100°C up to 100 atmospheres. This paper deal with the results of these measurements.

II. Apparatus and method

The apparatus and method used in the present paper are just the same as those in the preceding one,⁽⁶⁾ that is, the modified oscillating disc method with large axial separation of fixed plates, on which we have explained in detail in the last paper.

Logarithmic decrement was calculated from twenty successive oscillations. Period is the average of 21 oscillations measured by a stopwatch which could be read to 0.02 sec. A final logarithmic decrement and period for a given experimental condition were obtained by averaging the results from 3 or 4 runs. The manometer used was a large-sized Bourdon-type one, 8" in diameter, with 1 atm scale, covering the range from 0 to 300 atmospheres, which was calibrated with the standard pressure balance and could measure quite accurately to 0.1 atm.

As the test gas, commercial nitrogen and electrolysed hydrogen were used. Mixed gases to be measured were all purified passing through NH₃—NH₄Cl solution packed with copper nets, water, concentrated sulfuric acid and solid potassium hydroxide; they were dried, oxygen being eliminated. Nitrogen purified in this way had the purity of 99.6 per cent.

The density necessary for the calculation of viscosity from measured results was calculated using the compressibility measured by Holborn and Otto⁽⁷⁾ and by Otto, Michels and Wouters⁽⁸⁾ with nitrogen, and the one by Wiebe and Gaddy⁽⁹⁾ with the nitrogen and hydrogen system.

(4) J. H. Boyd, *Phys. Rev.*, **35** (1930), 1284.

(5) O. A. Uyehara and K. M. Watson, *Natl. Petroleum News*, **36** (1944), R 764.

(6) H. Iwasaki, *Sci. Rep. RITU, A* **3** (1951), 247.

(7) L. Holborn and J. Otto, *Z. Physik*, **33** (1925), 1.

(8) J. Otto, A. Michels and H. Wouters, *Phys. Z.*, **35** (1934), 97.

(9) R. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.*, **60**₂ (1938), 2300.

III. Experimental results

i) Apparatus constants. In the course of the experiment, the oscillating system was reassembled several times. Whenever it was reassembled determinations were made both on the apparatus constant C and the logarithmic decrement $2\pi\Delta_0$, caused by the internal friction of the suspension wire itself. The results of typical calculation of the apparatus constant are given in Table 1. The determination was made at 50°C and the measured values of nitrogen given by Michels and Gibson⁽¹⁰⁾ were used as standard viscosity values necessary for calculation, just as were in the preceding paper.

Table 1. Sample data for the calibration of the apparatus constant.

$$\Delta_0(B) = 0.00008_1$$

Exp. No.	Press.	ρ	Δ	T	T_0	$T_{0,mean}$	$\eta \cdot 10^6$	C	C_{mean}
C-1	54.5	0.0573 ₁	0.00542 ₂	9.409	9.358		197. ₅	0.546 ₉	
C-2	43.6	0.0459 ₃	0.00492 ₈	9.398	9.352	9.353	195. ₄	0.546 ₁	0.547 ₃
C-3	31.0	0.0327 ₁	0.00425 ₄	9.392	9.353		193. ₄	0.548 ₂	
C-4	20.6	0.0217 ₆	0.00361 ₉	9.384	9.350		191. ₉	0.548 ₀	

η^* : Values obtained from the interpolation of Michels & Gibson's data.⁽¹⁰⁾

Where pressure (p) given in the international atmospheres, density (ρ) in grams per cubic centimeter, the times (T, T_0) in seconds, and the viscosities (η) in c. g. s. units.

Apparatus constants at other temperatures were calculated from the measured values at 50°C and the expansion coefficient of discs. The oscillating systems used were 1) a disc, 0.925 mm thick, 28.0 mm in diameter (A), 2) the same as A, only reassembled in other way (B) and 3) one, 0.950 mm thick, 27.9₄ mm in diameter (C) (each kind was described in the table respectively), the material of which being V2A stainless steel, the suspension platinum wire 0.05 mm in diameter and about 182 mm long.

ii) The results of measurements are given in Tables 2—4.

From the calculation made by the observations from 3~4 runs made repeatedly under the same condition, it has been found out that the logarithmic decrement has no greater variation than 0.5 per cent.

It was confirmed that all the cautions^{†)} in this method had been fulfilled, that in consequence, the present experiment had been made under a satisfactory condition, and that the error had been less than 1 per cent.

The experiment on nitrogen at 25°C was made with the intention of reexamining the reliability of this method, and the measured values of this experiment were compared with those given by Michels and Gibson.⁽¹⁰⁾ The agreement is excellent as shown in Table 2 and we are sure that the present method is quite satisfactory.

†) *cf.* 6).

(10) A. Michels and R. O. Gibson, Proc. Roy. Soc., A 134 (1931), 288.

These experimental values were extrapolated to 1 atmosphere with following results: with nitrogen, at 100°C, $\eta_{1\text{atm}}=210.9 \cdot 10^{-6}$ (Kleint⁽¹¹⁾, $\eta_{1\text{atm}}=212.5 \cdot 10^{-6}$; Trautz and Baumann⁽¹²⁾, $\eta_{1\text{atm}}=208.5 \cdot 10^{-6}$), at 150°C, $\eta_{1\text{atm}}=229.0 \cdot 10^{-6}$ (Kleint, $\eta_{1\text{atm}}=233.0 \cdot 10^{-6}$; Trautz and Baumann, $\eta_{1\text{atm}}=228.1 \cdot 10^{-6}$), with 80.4% N₂—19.6% H₂ system, at 50°C, $\eta_{1\text{atm}}=184.3 \cdot 10^{-6}$ (Kleint, $\eta_{1\text{atm}}=186.7 \cdot 10^{-6}$; Trautz and Baumann, $\eta_{1\text{atm}}=184.1 \cdot 10^{-6}$), at 100°C, $\eta_{1\text{atm}}=206.9 \cdot 10^{-6}$ (Kleint, $\eta_{1\text{atm}}=208.0 \cdot 10^{-6}$; Trautz and Baumann, $\eta_{1\text{atm}}=205 \cdot 10^{-6}$), and lastly with 31.9% N₂—68.1% H₂ system, at 50°C, $\eta_{1\text{atm}}=160.5 \cdot 10^{-6}$ (Kleint, $\eta_{1\text{atm}}=163.4 \cdot 10^{-6}$; Trautz and Baumann, $\eta_{1\text{atm}}=158.0 \cdot 10^{-6}$), at 100°C, $\eta_{1\text{atm}}=176.0 \cdot 10^{-6}$ (Kleint, $\eta_{1\text{atm}}=178.0 \cdot 10^{-6}$). They agree fairly well with the viscosities of nitrogen and hydrogen system measured so far at the normal pressure.

Table 2. Experimental and calculated data for Nitrogen.

(25°C)									
$\Delta_0(\text{B}) = 0.00007_3$									
$C_{25^\circ\text{C}}(\text{B}) = 0.547_8$									
Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta^* \cdot 10^6$	$\eta \cdot 10^6$ Calc.
N-1	86.6	0.0991 ₁	0.00677 ₉	9.395	9.332		194.5	195.4	195.0
N-2	61.5	0.0706 ₅	0.00577 ₂	9.392	9.338		189.8	189.6	189.0
N-3	44.0	0.0506 ₀	0.00495 ₅	9.376	9.330		185.6	185.9	185.3
N-4	20.6	0.0236 ₇	0.00360 ₃	9.369	9.335		181.6	181.3	181.3
N-5	184.5	0.2020	0.01010 ₀	9.428	9.333	9.332	226.6	226.8	225.6
N-6	162.6	0.1804	0.00943 ₀	9.416	9.327		219.0	219.2	218.0
N-7	137.8	0.1548	0.00862 ₂	9.411	9.330		210.5	211.0	209.9
N-8	110.0	0.1250	0.00765 ₂	9.404	9.332		201.6	202.5	201.4
N-9	87.4	0.1000	0.00683 ₄	9.391	9.328		195.6	196.1	195.2

η^* : Values obtained from the interpolation of Michels & Gibson's data.⁽¹⁰⁾

(100°C)									
$\Delta_0(\text{A}) = 0.00010_3$									
$C_{100^\circ\text{C}}(\text{A}) = 0.542_2$									
Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta \cdot 10^6$ Calc.	
N-10	88.1	0.0784 ₃	0.00666 ₄	9.469	9.407		222.1	223.0	
N-11	61.9	0.0556 ₆	0.00572 ₄	9.454	9.400		218.5	218.6	
N-12	43.5	0.0393 ₆	0.00494 ₃	9.444	9.398		216.3	216.0	
N-13	20.6	0.0187 ₇	0.00368 ₉	9.434	9.400	9.402	212.2	213.0	
N-14	186.8	0.1582	0.00949 ₇	9.493	9.404		243.3	243.3	
N-15	162.5	0.1395	0.00890 ₇	9.483	9.399		239.0	237.8	
N-16	139.7	0.1214	0.00826 ₃	9.481	9.403		233.2	232.9	
N-17	109.6	0.0966 ₈	0.00738 ₃	9.474	9.404		227.4	226.9	

(150°C)									
$\Delta_0(\text{A}) = 0.00025_7$									
$C_{150^\circ\text{C}}(\text{A}) = 0.541_2$									
Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta \cdot 10^6$ Calc.	
N-18	109.5	0.0844 ₈	0.00740 ₂	9.555	9.487		242.3	242.3	
N-19	86.5	0.0674 ₇	0.00670 ₃	9.534	9.472		238.6	238.9	
N-20	61.3	0.0483 ₄	0.00582 ₈	9.525	9.472		235.5	235.5	
N-21	43.6	0.0346 ₃	0.00510 ₉	9.519	9.473		234.0	233.4	
N-22	20.7	0.0165 ₄	0.00393 ₃	9.510	9.475	9.475	234.6	230.9	
N-23	187.8	0.1391	0.00942 ₆	9.565	9.477		255.5	255.8	
N-24	162.7	0.1221	0.00880 ₄	9.555	9.473		249.5	251.2	
N-25	140.0	0.1064	0.00826 ₂	9.546	9.468		247.0	247.3	

(11) F. Kleint, Verh. deut. phys. Ges., 7 (1905), 146.

(12) M. Trautz and P. B. Baumann, Ann. Physik, [5] 2 (1929), 733.

Table 3. Experimental and calculated data for 80.4% N₂-19.6% H₂ system.

(50°C) $\Delta_0(B) = 0.00008_1$
 $C_{50^\circ C}(B) = 0.547_3$

Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta \cdot 10^6$ Calc.
N-H-1	20.6	0.0177 ₄	0.00329 ₄	9.386	9.356	9.356	186. ₀	186. ₃
N-H-2	44.1	0.0377 ₆	0.00446 ₁	9.397	9.356		189. ₄	189. ₂
N-H-3	61.5	0.0523 ₆	0.00513 ₈	9.403	9.355		191. ₇	191. ₈
N-H-4	83.5	0.0705 ₀	0.00588 ₅	9.408	9.354		195. ₂	195. ₄
N-H-5	107.5	0.0898 ₀	0.00661 ₃	9.416	9.354		199. ₆	199. ₉
N-H-6	121.5	0.1008	0.00701 ₄	9.420	9.355		202. ₉	202. ₆
N-H-7	147.0	0.1203	0.00767 ₂	9.434	9.362		207. ₉	208. ₁
N-H-8	162.6	0.1320	0.00805 ₁	9.432	9.357		210. ₄	211. ₅
N-H-9	177.1	0.1425	0.00839 ₇	9.433	9.354		213. ₅	214. ₉
N-H-10	190.4	0.1520	0.00873 ₇	9.439	9.357		218. ₂	218. ₂

(100°C) $\Delta_0(B) = 0.00010_3$
 $C_{100^\circ C}(B) = 0.546_3$

Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta \cdot 10^6$ Calc.
N-H-11	20.6	0.0153 ₂	0.00338 ₉	9.442	9.411	9.411	208. ₀	208. ₆
N-H-12	43.6	0.0321 ₄	0.00448 ₅	9.452	9.411		209. ₈	211. ₀
N-H-13	62.5	0.0457 ₂	0.00520 ₆	9.456	9.407		212. ₈	213. ₂
N-H-14	109.5	0.0783 ₅	0.00662 ₆	9.464	9.402		219. ₂	219. ₇
N-H-15	122.1	0.0868 ₀	0.00694 ₂	9.473	9.408		220. ₆	221. ₇
N-H-16	139.3	0.0981 ₅	0.00738 ₃	9.487	9.417		225. ₀	224. ₅
N-H-17	162.4	0.1130	0.00792 ₈	9.490	9.415		229. ₀	228. ₅
N-H-18	196.4	0.1341	0.00869 ₅	9.498	9.416		236. ₄	234. ₉

Table 4. Experimental and calculated data for 31.9% N₂-68.1% H₂ system.

(50°C) $\Delta_0(C) = 0.00009_2$
 $C_{50^\circ C}(C) = 0.553_6$

Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta \cdot 10^6$ Calc.
N-H-19	20.3	0.00781 ₉	0.00225 ₄	9.329	9.309	9.312	161. ₇	161. ₈
N-H-20	44.5	0.0169 ₄	0.00295 ₂	9.334	9.307		162. ₉	163. ₄
N-H-21	70.1	0.0263 ₃	0.00350 ₆	9.348	9.316		164. ₁	165. ₄
N-H-22	88.1	0.0327 ₈	0.00386 ₀	9.348	9.313		166. ₉	166. ₉
N-H-23	107.4	0.0395 ₃	0.00420 ₂	9.351	9.313		169. ₄	168. ₅
N-H-24	120.8	0.0441 ₂	0.00441 ₃	9.354	9.314		170. ₈	169. ₇
N-H-25	138.6	0.0501 ₁	0.00467 ₄	9.357	9.314		172. ₁	171. ₄
N-H-26	162.7	0.0579 ₉	0.00500 ₁	9.356	9.309		173. ₇	173. ₇
N-H-27	176.5	0.0623 ₉	0.00518 ₃	9.358	9.311		175. ₄	175. ₁
N-H-28	189.4	0.0664 ₃	0.00533 ₀	9.360	9.311		175. ₉	176. ₆

(100°C) $\Delta_0(C) = 0.00015_4$
 $C_{100^\circ C}(C) = 0.552_6$

Exp. No.	Press.	ρ	Δ	T	T_0	T_0 mean	$\eta \cdot 10^6$	$\eta \cdot 10^6$ Calc.
N-H-29	44.5	0.0146 ₆	0.00302 ₈	9.390	9.365	9.357	178. ₀	178. ₅
N-H-30	21.6	0.00719 ₇	0.00240 ₁	9.376	9.354		176. ₉	177. ₂
N-H-31	87.4	0.0281 ₅	0.00388 ₃	9.392	9.357		180. ₃	181. ₀
N-H-32	62.5	0.0204 ₀	0.00344 ₁	9.383	9.352		180. ₄	179. ₆

IV. Discussion

1. Relation between viscosity and pressure

Isotherms between measured viscosity and pressure are given in Figs. 1 and 2.

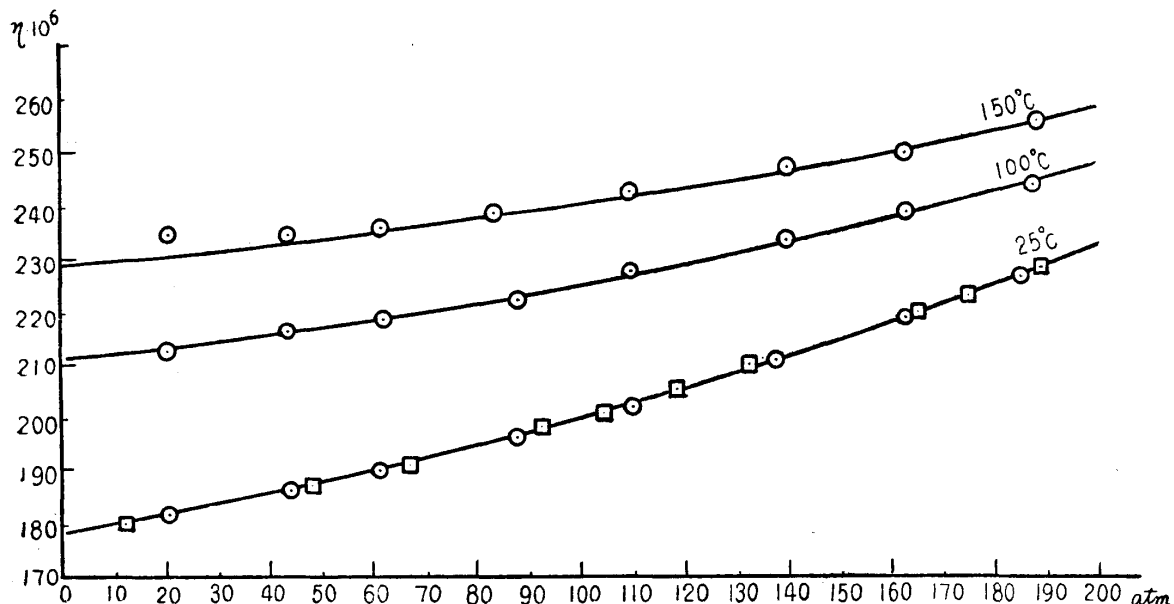


Fig. 1. Relation between Pressure and Viscosity of Nitrogen.

□: Values obtained by Michels & Gibson.⁽¹⁰⁾

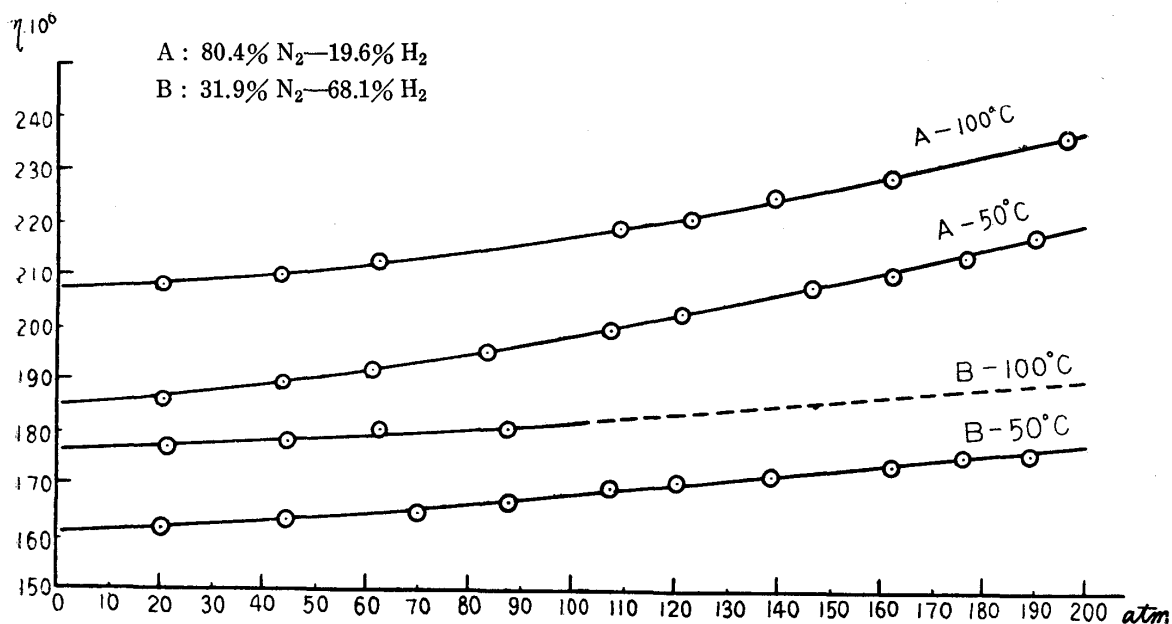


Fig. 2. Relation between Pressure and Viscosity of Binary Mixtures.

From these two figures, as in the case of air⁽⁶⁾, it is to be known that the lower temperature is, the greater $(\partial\eta/\partial p)_\theta$, the variation of viscosity with pressure, becomes and that as far as this experiment is concerned, $(\partial\eta/\partial\theta)_p > 0$ (θ : temperature). Furthermore, it is seen that $(\partial\eta/\partial p)_\theta$ decreases with the increase of the mole fraction of hydrogen.

2. Relation between viscosity and density

When isothermal curves are drawn of measured viscosities and density with each system, they all become equidistant one another within the experimental accuracy, so far as the present experiment is concerned. Fig. 3 is with nitrogen.

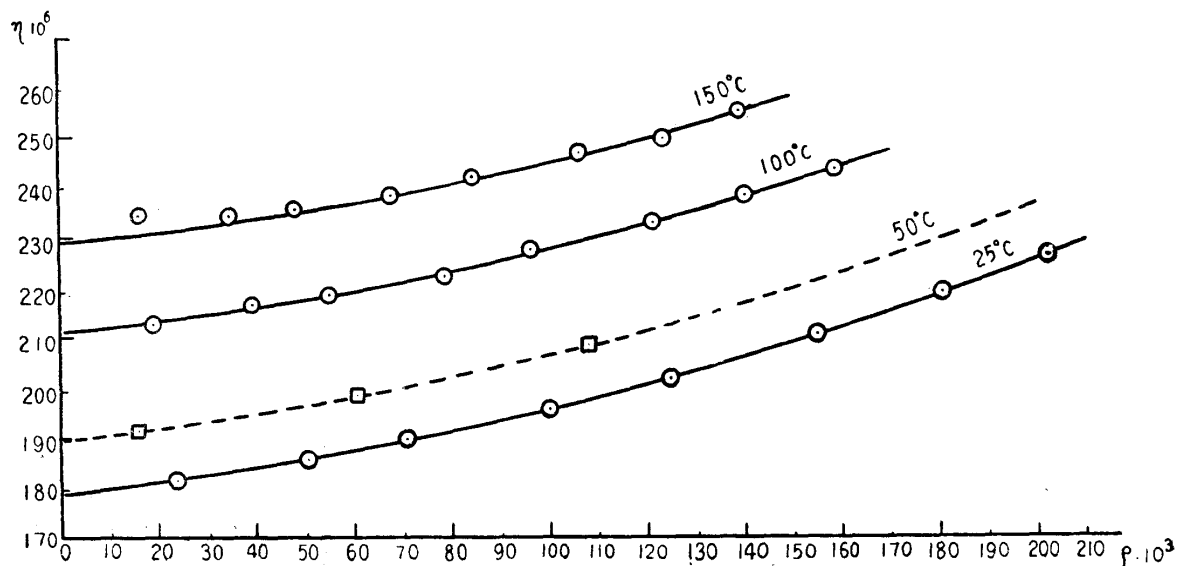


Fig. 3. Relation between Density and Viscosity of Nitrogen.

□: Values obtained by Michels & Gibson.

As viscosity, when density is quite small, approaches the one at a normal pressure, it may generally expand to the power of density ρ .

That is,

$$\eta = \eta_0 + \alpha\rho + \beta\rho^2 + \dots\dots\dots,$$

where η_0 is the viscosity at a normal pressure and, α and β are constants.

At the same time, taking into consideration of the above-mentioned experimental results in which isotherms of viscosity and density become equidistant one another, we can calculate the α , β and η_0 in the above equation using the measured values as follows:

with N_2 system,

$$\eta_{\rho,t} = \eta_{0,t} + 0.000103\rho + 0.000643\rho^2, \quad (1)$$

with 80.4% N_2 -19.6% H_2 system,

$$\eta_{\rho,t} = \eta_{0,t} + 0.000101\rho + 0.000800\rho^2, \quad (2)$$

and with 31.9% N_2 -68.1% H_2 system,

$$\eta_{\rho,t} = \eta_{0,t} + 0.000152\rho + 0.00130\rho^2. \quad (3)$$

The above-mentioned values of η_{1atm} show those of η_0 obtained by the above method.

The viscosities ($\eta_{Calc.}$) calculated from those equations, using the values given above for $\eta_{0,t}$, are listed in the last columns of Tables 2-4. It is to be added that as η_0 at 25°C with nitrogen was taken $178.5 \cdot 10^{-6}$, not the extrapolated value $177.5 \cdot 10^{-6}$ given by Michels and Gibson. So is with the following calculations.

From this, as far as the present experiment is concerned, it is seen that the

equation to the term of the second order in ρ above-mentioned is in good agreement with the experimental results. Further, with nitrogen, the above equation can show the experimental results pretty well, as far as the vicinity of the critical density ($\rho_c=0.311$ g/cc), which fact was confirmed by comparing with the values measured by Michels and Gibson. Those results are given in Table 5.

Table 5. Comparison of measured and calculated values of viscosity of nitrogen up to the critical density region.

25°C				50°C				75°C			
p	ρ	$\eta^{(a)} \cdot 10^6$	$\eta \cdot 10^6$ Calc.	p	ρ	$\eta^{(a)} \cdot 10^6$	$\eta \cdot 10^6$ Calc.	p	ρ	$\eta^{(a)} \cdot 10^6$	$\eta \cdot 10^6$ Calc.
14.44	0.01659	180.0	180. ₄	15.37	0.01623	191.3	191. ₅	15.37	0.01505	202.2	201. ₈
48.22	0.05549	186.4	186. ₂	57.60	0.06049	198.1	198. ₅	57.61	0.05591	208.8	207. ₈
104.5	0.1190	200.5	199. ₉	104.5	0.1083	208.8	208. ₃	104.5	0.09970	217.5	216. ₇
212.4	0.2300	236.7	236. ₃	212.4	0.2067	237.3	238. ₅	212.4	0.1902	240.8	242. ₉
320.4	0.3141	276.4	274. ₃	320.4	0.2875	273.7	272. ₅	320.3	0.2659	274.6	273. ₂

(a) Measured values by Michels & Gibson.⁽¹⁰⁾

The broken line in Fig. 3 was drawn from Eq. (1), using the extrapolated value $\eta_0 = 189.6 \cdot 10^{-6}$ to 1 atmosphere, measured on nitrogen at 50°C by Michels and Gibson; the values shown as \square in the same figure give those measured by them. The broken line of B-100°C in Fig. 2 was calculated from Eq. (3).

3. Relation*) between viscosity and components

The relation between viscosity and components at a given temperature and pressure is shown in the next equation:

$$\eta_m = n_N \eta_N + n_H \eta_H + A_{(\eta)},$$

where η_m showing the viscosities of mixed gases containing n_N and n_H mole fractions of nitrogen and hydrogen respectively; η_N and η_H the viscosities of pure nitrogen and hydrogen at the same temperature and pressure.

In showing the viscosities of mixed gases in this way, it is naturally considered that $A_{(\eta)}$ depends on the components, temperature and pressure. Next, making use of the above experimental results, we shall examine the influence of the pressure on $A_{(\eta)}$, at 50° and 100°C respectively. Thinking, however, that in so far as the experimental conditions are concerned, the above-mentioned relation between viscosity and density is also true of the viscosity of pure hydrogen, we used the values calculated from the measured values up to 300 atmospheres at 25°C given by Gibson⁽¹³⁾ and the interpolated values at 50° and 100°C from those at a normal pressure given by Trautz and Kurz⁽¹⁴⁾ and by Sutherland and O. Maass⁽¹⁵⁾ respectively. The solid lines in Fig. 4 show the isotherms of viscosity and density of hydrogen. The values measured by Kuss⁽¹⁶⁾ at 25°, 50° and 75°C are given in

*) Viscosities used in the examination of this relation were calculated from Eqs. (1)~(3).

With hydrogen, those values obtained from the under-mentioned viscosity-density curves.

(13) R. O. Gibson, Diss. Amsterdam (1933); Landolt, Erg. IIIa, 189.

(14) M. Trautz and F. Kurz, Ann. Physik, [5] 9 (1931), 981.

(15) B. P. Sutherland and O. Maass, Canad. J. Research, 6 (1932), 428.

(16) E. Kuss, Z. angew. Physik, 4 (1952), 203.

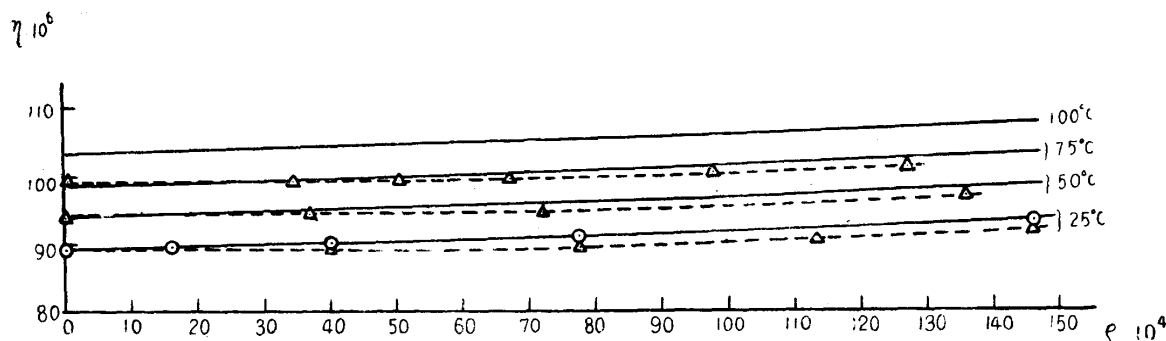


Fig. 4. Relation between Density and Viscosity of Hydrogen.

○ Values obtained by Gibson.

△ Values obtained by Kuss.

the broken lines. His isotherms themselves are equidistant one another, but it is seen from the experimental accuracy of 2 per cent that they are in agreement with the above calculation.

From the above-mentioned experimental results, the relation between $\Delta_{(\eta)}$ and pressure was calculated, the results of which are given in Table 6.

Table 6. Calculation of $\Delta_{(\eta)}$.
(50°C)

p	$\eta_N \cdot 10^6$	$\eta_H \cdot 10^6$	80.4% N ₂ -19.6% H ₂		$\Delta_{(\eta)} \cdot 10^6$	31.9% N ₂ -68.1% H ₂		$\Delta_{(\eta)} \cdot 10^6$
			$\eta_m \cdot 10^6$	$(n_N \eta_N + n_H \eta_H) \cdot 10^6$		$\eta_m \cdot 10^6$	$(n_N \eta_N + n_H \eta_H) \cdot 10^6$	
1	189.6	93.8	184.3	170.8	13.5	160.5	124.4	36.1
50	196.8	95.2	190.1	176.9	13.2	163.9	127.6	36.3
100	207.2	96.3	198.4	185.5	12.9	167.9	131.7	36.2
150	220.2	97.3	208.7	196.1	12.6	172.5	136.5	36.0
200	235.0	98.3	220.4	208.2	12.2	177.4	141.9	35.5

(100°C)

p	$\eta_N \cdot 10^6$	$\eta_H \cdot 10^6$	80.4% N ₂ -19.6% H ₂		$\Delta_{(\eta)} \cdot 10^6$	31.9% N ₂ -68.1% H ₂		$\Delta_{(\eta)} \cdot 10^6$
			$\eta_m \cdot 10^6$	$(n_N \eta_N + n_H \eta_H) \cdot 10^6$		$\eta_m \cdot 10^6$	$(n_N \eta_N + n_H \eta_H) \cdot 10^6$	
1	210.9	103.0	206.9	189.8	17.1	176.0	137.4	38.6
50	216.9	104.0	211.7	194.8	16.9	178.9	140.0	38.9
100	225.0	104.9	218.3	201.5	16.8	182.2	143.2	39.0
150	235.1	106.0	226.3	209.8	16.5	(185.9)*	147.2	(38.7)
200	246.4	106.8	235.6	219.0	16.6	(190.0)*	151.3	(38.7)

* Values extrapolated by Eq. (3).

According to this table, it is to be seen that $\Delta_{(\eta)}$ is the function of components and temperature and that it is quite independent of pressure with the experimental accuracy.

Thus, the isobaric curves of viscosity and components of binary mixtures can be drawn from the relation between viscosity and components at 1 atmosphere and the one between viscosity and pressure of each component, in accordance with the accuracy of them.

From these results, the isobaric curve at 1 atmosphere was drawn from the theoretical formulas by Hirschfelder *et al.*^{(17) *}, and so $\Delta(\eta)$ was calculated from this curve. Their theoretical formulas show that they are in good agreement with the measured values of many systems; moreover, as is seen from the figures to be given later, they agree fairly well with the extrapolated values of the present author. The isobaric curves at every 50 atmospheres at 50° and 100°C are given in Figs. 5 and 6, drawn from the above $\Delta(\eta)$ and the viscosities at high

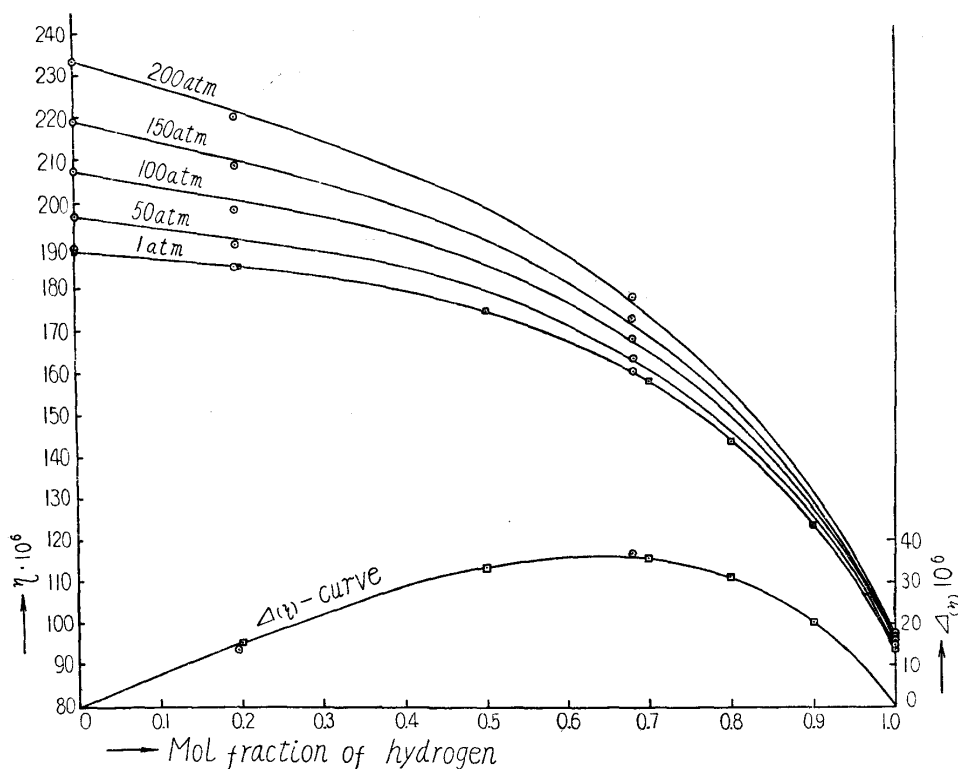


Fig. 5. Viscosity isobar of nitrogen and hydrogen system as a function of mole fraction of hydrogen at 50°C.

pressure of each component. At the lower part of each figure, $\Delta(\eta)$ -curve was drawn at respective temperature. But the isobaric curves at 1 atmosphere were drawn from the calculation by the theoretical formulas of Hirschfelder *et al.* The sign of \square in the figures shows their calculated values; that of \odot is the values measured by the present author. From Figs. 5 and 6, it is seen that so far as the present experiment is concerned, the isobaric curves drawn in this way agree with the measured values within the error of about 1 per cent.

Moreover, seeing that the viscosities $\eta_{150 \text{ atm}} = 186.2 \cdot 10^{-6}$ and $\eta_{200 \text{ atm}} = 191.0 \cdot 10^{-6}$ of 31.9% N_2 -68.1% H_2 system obtained from Fig. 6 are in good agreement with those from the broken line of B-100°C in Fig. 2, namely $185.9 \cdot 10^{-6}$, and $190.0 \cdot 10^{-6}$, values calculated from Eq. (3), it is estimated that the broken line of B-100°C shows the true viscosity.

(17) J. O. Hirschfelder, R. B. Bird and E. L. Spatz, *Chem. Rev.*, **44** (1949), 205.

*) After their method, we used the values of force constants between like molecules obtained from viscosity and those between dissimilar ones got from diffusion.

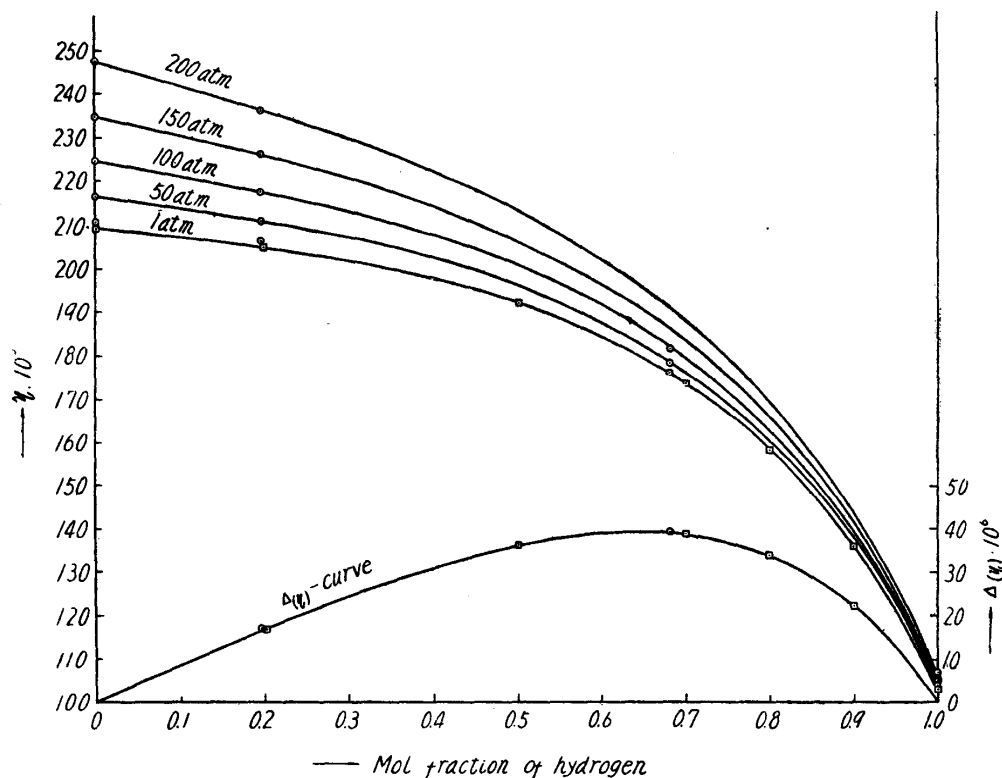


Fig. 6. Viscosity isobar of nitrogen and hydrogen system as a function of mole fraction of hydrogen at 100°C.

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Note

For lack of the data, the correlation curves, according to the theorem of corresponding states, have so far been drawn only as far as the vicinity of $T_r (= T/T_c) \cong 3.0$, and no reliable curves have been drawn for higher T_r .

Therefore, making use of the above experimental results as well as the viscosities of hydrogen measured by Gibson and Kuss, respectively, we drew correlation curves in a figure, after Comings and Egly, and succeeded in expanding the upper limit ($T_r = 2.80$) of the reduced temperature given in their curves to $T_r = 7.25$.

With mixtures of nitrogen and hydrogen, it is seen that we can predict their viscosities with the error of about 1 per cent by the same $\eta/\eta_0 \cdot P_r \cdot T_r$ curves.

And within the range of temperature given in this figure, it may be said there are scarcely any experimental values to be compared except those of the present author about air at 150°C. The values obtained from this figure are seen to agree with them within the error of 1~2 per cent.

As the critical constants of mixtures, we used the pseudo-critical constants derived from the molal average of the critical constants of each component.

Needless to say, with hydrogen, as is generally done, the critical temperature T_c (°K) and critical pressure P_c (atm) were used, adding 8 to the real value.

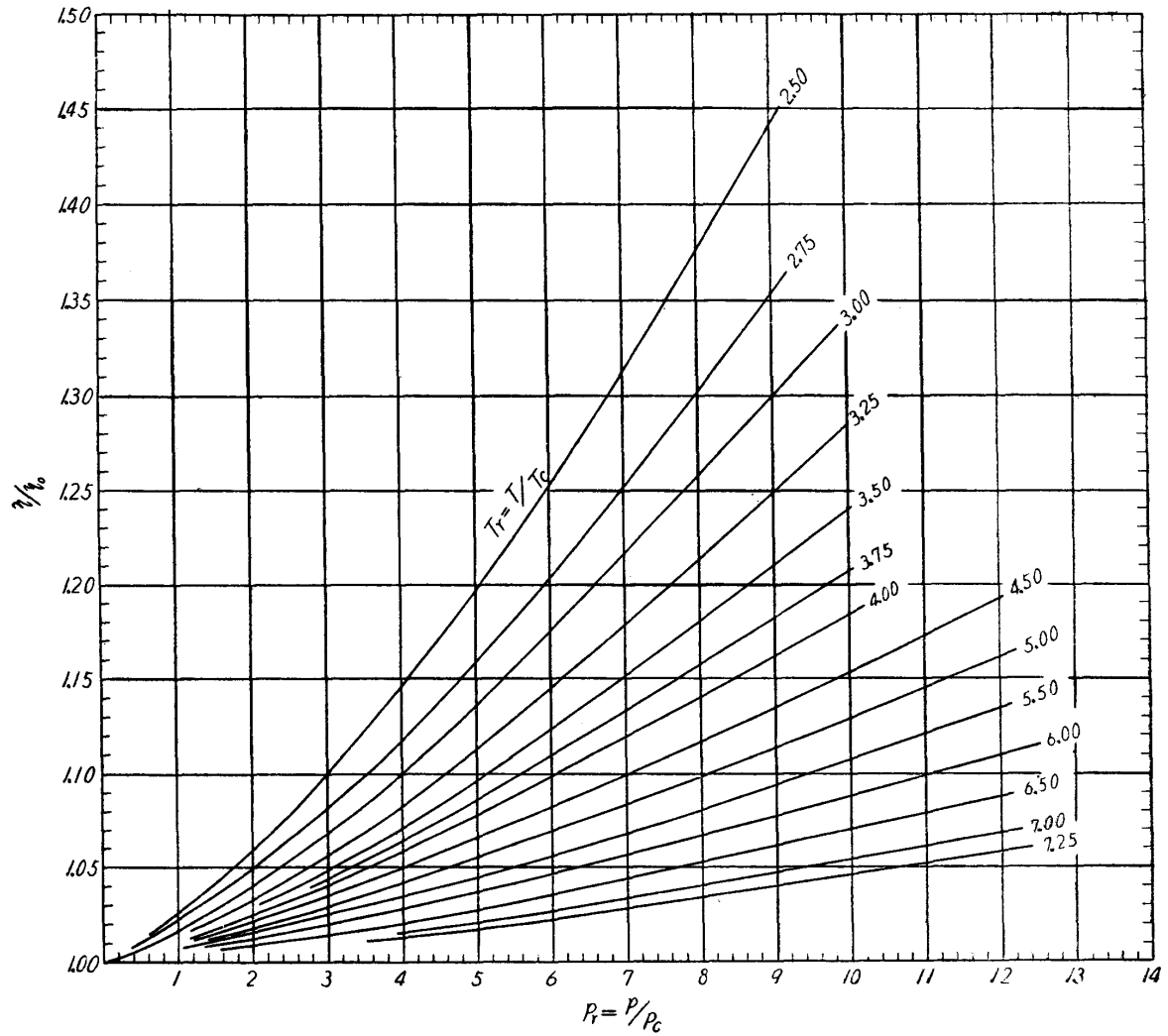


Fig. 7. Generalized Reduced Viscosities.