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STUDIES ON THE TRANSPORT PROPERTIES OF FLUIDS AT HIGH PRESSURE

I The Viscosity of Ammonia*

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The viscosity of ammonia was measured at temperatures of 25, 50, 75, 100 and 125°C over the pressure range from 1 atm to near the saturation pressure, using the oscillating disk method. Also, an experiment at 135°C was carried out only to see the initial density dependency of the viscosity of ammonia. The accuracy of the measurements is estimated to be ±0.3%.

It is found that at 25, 50 and 75°C the viscosity of ammonia shows a steady decrease with an increase in pressure (or density), and that at 100 and 125°C it passes through a minimum.

The data were fitted to the polynomials of density at each temperature investigated. The coefficient of the first order density term in the equation, which indicates the degree of the initial density dependency, shows a decrease in its absolute value with an increase in temperature under the present experimental conditions and becomes zero at about 135°C.

Introduction

Many reliable papers on the viscosity of gases at high pressures have been published, but most of them are on non-polar gases. On the other hand, papers on the effect of pressure on the viscosity of polar gases are very few, so far. Investigations of the effect of pressure on the viscosity of ammonia have been made by several investigators1)~5), but the results have not indicated any definite relation between the viscosity of ammonia and the pressure (or density). Therefore, the measurements of the viscosity of ammonia were undertaken at several temperatures in the range from 25 to 135°C over the pressure range from 1 atm to near the saturation pressure.

Experimentals

Method

Measurements were made by the Maxwell type oscillating disk method.

The suspension system used in this investigation is almost the same as that in previous paper6),

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1) L. T. Carmichael, H. H. Reamer and B. H. Sage, *J. Chem. Eng. Data*, **8**, 400 (1963)
2) H. Iwasaki, J. Kestin and A. Nagashima, *J. Chem. Phys.*, **40**, 2988 (1964)
3) T. Makita, *The Memoirs of the Faculty of Ind. Arts, Kyoto Tech. Univ., Science and Technology*, **4**, 19 (1955)
4) H. Z. Stakelbeck, *Z. Ges. Kälte-Ind.*, **40**, 33 (1933)
5) H. Shimotake and G. Thodos, *A.I.Ch.E.J.*, **9**, 68 (1963)
6) H. Iwasaki and H. Takahashi, *Bull. Chem. Res. Institute of Non-Aqueous Solutions, Tohoku Univ.*, **6**, 61 (1956)

except for some modification of the methods of the fastening of the quartz wire to the steel rod and the steel rod to the oscillating disk. The quartz wire was prepared as follows. First, a quartz rod, 20 cm long and about 0.3 mm in diameter, was drawn from a piece of clear, fused quartz, care being taken that its diameter was uniform throughout the length of the rod. And, then, the quartz rod was treated with hydrogen fluoride to obtain a uniformly thin wire, 18.5 cm long and about 35 μ in diameter, keeping off

Table 1 Characteristics of suspension system (25°C)

Total separation between plates	$D=0.1732_4$ cm	
Upper separation	$b_1=0.0386_6$ cm	
Lower separation	$b_2=0.0386_6$ cm	
Radius of disk	$R=1.3955_7$ cm	
Thickness of disk	$d=0.0959_1$ cm	
Moment of inertia of suspension system	$I=4.5119$ g·cm^2	
Damping decrement/natural period of oscillation	at 25°C	$\Delta_0/T_0=0.91\times10^{-6}$
	at 50°C	$\Delta_0/T_0=0.96\times10^{-6}$
	at 75°C	$\Delta_0/T_0=1.51\times10^{-6}$
	at 100°C	$\Delta_0/T_0=2.53\times10^{-6}$
	at 125°C	$\Delta_0/T_0=4.23\times10^{-6}$
	at 135°C	$\Delta_0/T_0=5.24\times10^{-6}$

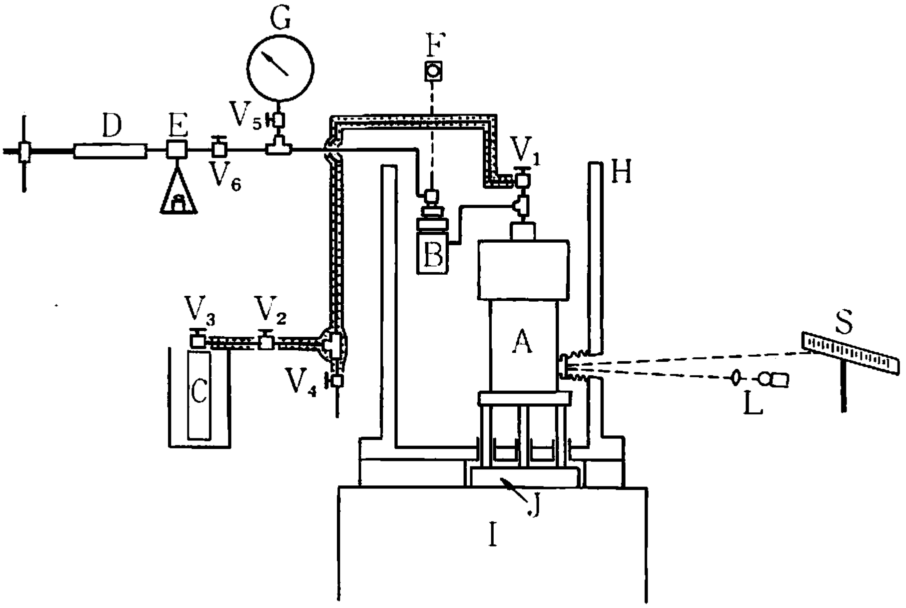

Fig. 1 Schematic diagram of the apparatus

A: viscometer
B: detector for balancing of pressure
C: ammonia storage cylinder
D: oil pump
E: pressure balance
F: pilot lamp
G: pressure gauge
H: thermostat
I, J: base
L: light source
S: scale
V: valves

both ends of the rod from the contact with hydrogen fluoride solution. Both ends of the quartz strand prepared thus were plated with silver and with copper by turns. One end of the quartz strand, 5 mm long, was soldered to the thin stainless steel rod, 12 mm long, which was screwed perpendicularly on the oscillating disk. The other end, 10 mm long, was also soldered to the stainless steel holder fixed to the top plate of the suspension system.

Great care was taken in aligning the suspension system itself by ensuring good parallelism of the fixed plates and the oscillating disk and, moreover, the change of the relative position of the oscillating disk between the fixed plates with the change of temperature was made as small as possible using the quartz tube and quartz suspension wire as shown in Fig. 2 of ref. 6). The characteristics of the suspension system are recorded in Table 1.

In Fig. 1 the schematic diagram of the apparatus is shown. The viscometer was mounted in the thermostat H. The two lines were connected with the viscometer. One is the sample line and the other is that for measuring pressure. C, the ammonia storage cylinder, is mounted in the thermo-bath. B, the detector for balancing of pressure, is equipped with the bellows, mercury and the electric needle as shown in Fig. 2. The line from the inside of the bellows in B to the oil pump D was filled with oil and the outside of the bellows in B was linked with the viscometer.

The pressure was measured with an accuracy of 0.01 atm by means of a Bourdon gauge up to 11 atm and by a pressure balance of the free piston type for the pressures above 11 atm. The Bourdon

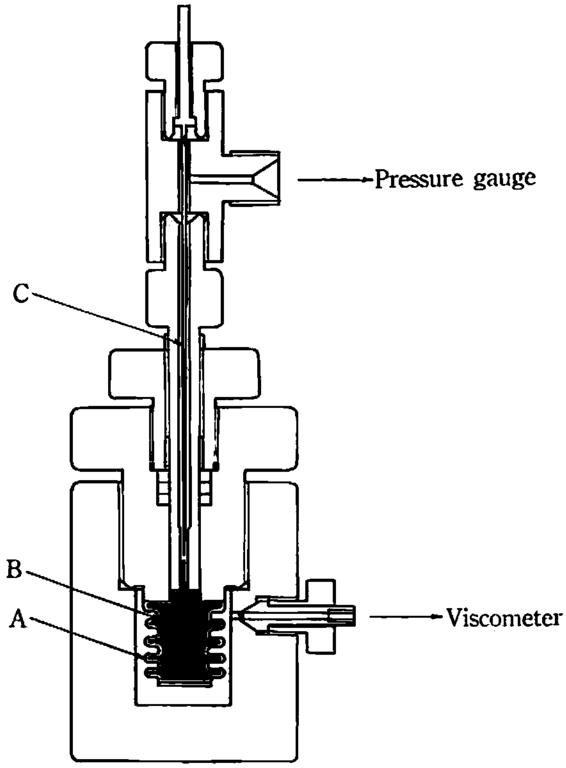

Fig. 2 Detector
A : bellows
B : mercury
C : electric needle

gauge was calibrated against a mercury column pressure gauge. The sensitivity of the pressure balance is 0.002 atm. The detector was sensitive to 10 mmHg.

The temperature of the thermostat H was kept constant within ±0.01°C and it was measured with an uncertainty of ±0.01°C by means of a mercury glass thermometer. However, above 100°C the temperature distribution through the thermostat was maintained constant at the value better than 0.02°C.

Material

The ammonia sample was dried and purified by distillation from metallic sodium and redistillation six times.

Evaluation of results

According to Newell's theory the results of measurements are evaluated by following equations (1) and (2) using the measured values of logarithmic decrement Δ and period of oscillation T[7][8].

$$\eta=\frac{2\pi\rho b^2}{\beta^2 T_0} \tag{1}$$

where $\beta=b/\delta$.

$$C_N=\left[\frac{2I}{\pi\rho b R^4}\left(\frac{\Delta}{\tau}-\Delta_0\right)+a\frac{\Delta}{\tau}\right]\beta^2+f\frac{3\Delta^2-1}{\tau^2}\beta^4+h\frac{\Delta(\Delta^2-1)}{\tau^3}\beta^6 \tag{2}$$

where $a=2/3$, $f=1/45$ and $h=8/945$, if $b_1=b_2$.

Here, the constant C_N which characterizes the effect of the edges and corners of the disk upon the oscillation is given by equation (3).

$$C_N=1+\frac{8b}{\pi R}[\cosh\gamma\cdot\ln(\cosh\gamma+1)-(\cosh\gamma-1)\cdot\ln\sinh\gamma]+2\left(\frac{b}{R}\right)^2\left(1+\frac{3d}{2b}-N(r)\right) \tag{3}$$

where $\gamma=\cosh^{-1}(1+r)$, $r=d/2b$.

If the terms containing a, f and h in equation (2) are neglected, equations (1) and (2) can be combined to give equation (4).

$$\eta=\frac{4Ib}{C_N R^4}\left(\frac{\Delta}{T}-\frac{\Delta_0}{T_0}\right)=K\left(\frac{\Delta}{T}-\frac{\Delta_0}{T_0}\right) \tag{4}$$

The accuracy of the present experiments is at least ±0.3% considering the uncertainty of determination of Δ, the effect of the change of the relative position of the oscillating disk with the change of temperature on the apparatus constant, and other sources of error. Also, it is known from the present experiments that equation (4) can be used satisfactorily, within the experimental error, under the present experimental conditions. Then, evaluations of the measurement results were carried out using equation (4) in the present experiments. Although the uncertainties in determination of viscosities are better than ±0.3%, it is considered that the relative values in the lower pressure region at each temperature,

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7) G. F. Newell, *ZAMP*, **10**, 160 (1959)

8) H. Iwasaki and J. Kestin, *Physica*, **29**, 1345 (1963)

where the initial density dependency of the viscosity is determined, are even more precise, with an uncertainty not exceeding ±0.1%, because all systematic errors tend to be the same in the lower pressure region at each temperature.

Equations (1), (2) and (3) are derived under the conditions of $D \ll R$ and $D \ll \delta$, but it is known from the research by Kestin and Leidenfrost[9] and that by Iwasaki and Kestin[8] that these equations can be used with an accuracy of ±0.1% under the conditions of $\delta/b \geqslant$ about 1.25 when $D/R \fallingdotseq 0.1$. And, of course, the motion of the fluid should be laminar and the condition of laminar motion is given by Foch and Barriol as $Re=(a\omega R^2)/\nu<60$. It was confirmed that the present measurements satisfactorily fulfill the conditions mentioned above. For example, the experimental results at 125°C were shown in Table 2. All of the values δ/b were larger than 1.2.

The calibration measurements of the apparatus constant K were made using air at 1 atm and 25°C, since Bearden's value[10] of 181.92±0.006 μ poise at 1 atm and 20°C is still considered to be what is best available. Here, the temperature correction for the viscosity of air was taken as 0.494 μ poise/°C[11].

Table 2 Experimental results at 125°C

Pressure P atm	Density ρ g/cm³	Period T sec	Decrement $\Delta \cdot 10^2$	Viscosity η μ poise	Boundary-layer thickness δ cm	δ/b
1.00	0.000523	26.588	2.2977	139.5	1.06	27.31
1.56	0.00081	26.591	2.2906	139.3	0.849	21.96
2.62	0.00137	26.598	2.2916	139.3	0.655	16.94
4.22	0.00223	26.600	2.2913	139.3	0.514	13.30
5.22	0.00276	26.606	2.2914	1.393	0.461	11.95
6.11	0.00321	26.602	2.2884	139.1	0.428	11.07
8.07	0.00432	26.595	2.2908	139.3	0.369	9.54
9.36	0.00503	26.606	2.2865	139.0	0.342	8.85
12.64	0.00689	26.613	2.2861	138.9	0.292	7.55
15.41	0.00849	26.619	2.2827	138.7	0.263	6.80
17.77	0.00988	26.625	2.2881	139.0	0.244	6.31
19.88	0.01115	26.620	2.2868	138.9	0.230	5.95
23.65	0.01349	26.625	2.2861	138.9	0.209	5.41
24.10	0.01377	26.610	2.2884	139.1	0.207	5.35
27.93	0.01624	26.628	2.2916	139.2	0.190	4.91
32.31	0.01918	26.636	2.2939	139.3	0.175	4.53
38.00	0.02322	26.636	2.2977	139.5	0.159	4.11
40.41	0.02503	26.644	2.3033	139.8	0.154	3.98
44.58	0.02825	26.627	2.3037	139.9	0.145	3.75
48.40	0.03138	26.645	2.3114	140.3	0.138	3.57
54.31	0.03655	26.647	2.3264	141.2	0.128	3.31
59.70	0.04171	26.652	2.3460	142.4	0.120	3.10
65.77	0.04816	26.656	2.3662	143.6	0.112	2.90
71.31	0.05477	26.669	2.3988	145.5	0.106	2.74
77.28	0.06301	26.675	2.4376	147.8	0.100	2.59
81.99	0.07057	26.681	2.4759	150.1	0.095	2.46
85.32	0.07687	26.685	2.5146	152.5	0.092	2.38
86.96	0.08031	26.679	2.5409	154.1	0.090	2.33
92.18	0.09418	26.690	2.6235	159.1	0.085	2.20

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9) J. Kestin and W. Leidenfrost, *Physica*, **25**, 1033 (1959)

10) J. A. Bearden, *Phys. Rev.*, **56**, 1023 (1939)

11) "Jikken Kagaku Koza" continued, Vol. 1. p. 350, ed. by Chem. Soc. Japan, (1966)

Also, calibration was made by means of nitrogen at 1 atm and 25°C, using the value proposed by Kestin and Whitelaw[12]. The values of K obtained by both methods showed good agreement, the discrepancy being 0.04%. The values of K at other temperatures can be evaluated by the knowledge of the expansion coefficient of the material of the suspension system.

Results

The experimental results are presented in Table 3. The density of ammonia was calculated using the compressibility data given by Date[13].

The experimental results have been represented graphically in Figs. 3 and 4. The diagram in Fig. 3 represents the variation of the viscosity of ammonia with pressure for the temperatures. The

Table 3 Experimental results

Pressure atm	Density g/cc	Viscosity μ poise	Pressure atm	Density g/cc	Viscosity μ poise
	25°C			50°C (continued)	
1.00	0.000704	100.7	10.97	0.00774	108.4
2.21	0.00157_6	100.4	11.45_7	0.00812_7	108.2
3.13	0.00225_6	100.1	12.03_1	0.00858_6	108.1
4.09	0.00298_2	99.6	13.84_7	0.01008_2	107.8
5.16	0.00381	99.2	14.63_0	0.01075_1	107.6
5.21	0.00385	99.2	15.51_9	0.01152_5	107.2
6.09	0.00456	98.8	17.39_3	0.01323_1	106.9
7.16	0.00545	98.5	18.30_5	0.01410_3	106.8
8.14	0.00629	98.2	19.30_5	0.01512_2	106.5
8.35	0.00648	98.2	19.72_1	0.01568_7	106.7
9.56	0.00763	97.8		75°C	
9.72	0.00783	97.7	1.00	0.000599	120.0
	50°C		2.10	0.00126_7	119.7
1.00	0.000646	110.4	3.23	0.00196_0	119.5
1.54	0.00100_0	110.3	5.08	0.00311_6	119.3
2.07	0.00135_0	110.2	6.43	0.00397_6	119.2
2.10	0.00137_1	110.2	8.74	0.00548_5	118.8
2.61	0.00170_7	110.0	11.09	0.00707_1	118.5
3.50	0.00231_0	109.8	13.99_5	0.00911_5	118.2
4.09	0.00271_2	109.6	16.54_6	0.01099_2	118.1
5.16	0.00345	109.4	19.53_2	0.01329_4	117.7
5.99	0.00403	109.2	23.06_3	0.01618_6	117.6
7.21	0.00491	109.0	25.73_3	0.01852_5	117.5
8.06	0.00553	108.8	28.63_4	0.02122_5	117.4
9.03	0.00625	108.7	32.92_2	0.02564_3	117.3
9.92	0.00693	108.6	34.98_5	0.02804_3	117.3
10.36	0.00726	108.4			

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12) J. Kestin and J. H. Whitelaw, *Physica*, **29**, 335 (1963)

13) K. Date, *unpublished data*. Values at 135°C were evaluated using Beattie-Bridgeman equation.

Table 3 (continued)

Pressure atm	Density g/cc	Viscosity μ poise	Pressure atm	Density g/cc	Viscosity μ poise
	100°C			125°C (continued)	
1.00	0.000558	129.9	24.10_5	0.01377_7	139.1
2.05	0.00115_2	129.8	27.93_7	0.01624_5	139.2
3.13	0.00176_4	129.6	32.31_4	0.01918_1	139.3
4.56	0.00258_1	129.7	38.00_4	0.02322_6	139.5
6.01	0.00344	129.5	40.41_8	0.02503_1	139.8
8.55	0.00494	129.3	44.58_0	0.02825_1	139.9
11.47	0.00672	129.2	48.40_3	0.03138_2	140.3
14.98_2	0.00894_4	129.0	54.31_4	0.03655_5	141.2
18.27_4	0.01110_7	128.8	59.70_2	0.04171_8	142.4
23.48_1	0.01471_9	128.6	65.77_9	0.04816_8	143.6
30.23_5	0.01981_3	128.6	71.31_5	0.05477_2	145.5
35.96_0	0.02456_7	128.9	77.28_3	0.06301_6	147.8
43.58_5	0.03173_7	129.4	81.99_1	0.07057_7	150.1
47.94_9	0.03639_3	129.9	85.32_0	0.07687_1	152.5
55.11_9	0.04539_5	131.2	86.96_0	0.08031_9	154.1
59.75_9	0.05265_7	132.4	92.18_4	0.09418_6	159.1
	125°C			135°C	
1.00	0.000523	139.5	1.00	0.000510	143.2
1.56	0.000817	139.3	1.75	0.00089_5	143.2
2.62	0.00137_8	139.4	2.20	0.00112_7	143.2
4.22	0.00223_1	139.3	2.95	0.00151_4	143.3
5.22	0.00276_9	139.3	4.00	0.00206_0	143.1
6.11	0.00321_8	139.1	5.15	0.00266_7	143.2
8.07	0.00432_4	139.3	5.99	0.00310_5	143.2
9.36	0.00503_9	139.0	7.28	0.00379_0	143.3
12.64_3	0.00689_3	138.9	9.15	0.00479_3	143.3
17.77_2	0.00988_6	139.0	11.69_0	0.00617_5	143.3
19.88_4	0.01115_7	138.9	13.17_6	0.00699_5	143.3
23.65_9	0.01349_2	138.9			

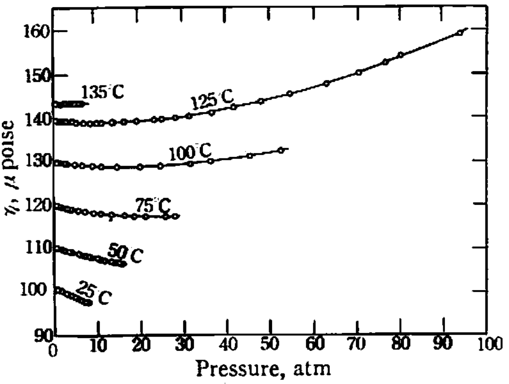

Fig. 3 Effect of pressure on viscosity of ammonia

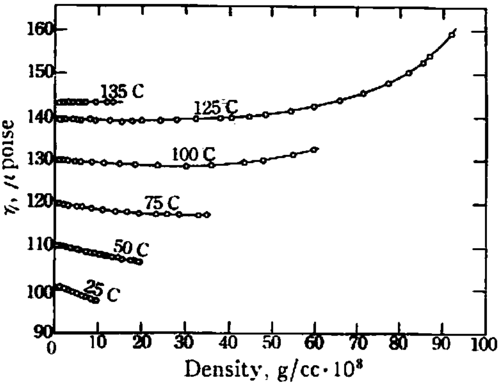

Fig. 4 Effect of density on viscosity of ammonia

viscosity of ammonia shows a steady decrease with pressure at the temperature from 25 to 75°C. However, the viscosities at 100 and 125°C pass through a minimum. The experiment at 135°C was carried out only to see the initial pressure or density dependency of the viscosity of ammonia. The diagram in Fig. 4 representing the variation of the viscosity of ammonia with density shows exactly the same tendency as that in Fig. 3.

From Figs. 3 and 4 it is observed that the negative pressure or density dependency of the viscosity of ammonia changes gradually with temperature to zero at about 135°C. under the experimental conditions. This relation is clarified by representing the viscosity of ammonia in the polynomials of

Table 4 Values of constants in equation (5) *

Temp. °C	η_0	b	$c\cdot10^3$	$d\cdot10^6$
25	101.0_5	−0.496	9.0	………
50	1.105_6	−0.383	9.0	………
75	120.0_8	−0.273	9.07	−104
100	129.9_8	−0.133	3.50	………
125	139.4_5	−0.0720	3.67	−7.03
135	143.2_1	0.01		

* $\eta=\eta_0+b\rho+c\rho^2+d\rho^3$ η: μpoise, ρ: g/10³cc (g/l)

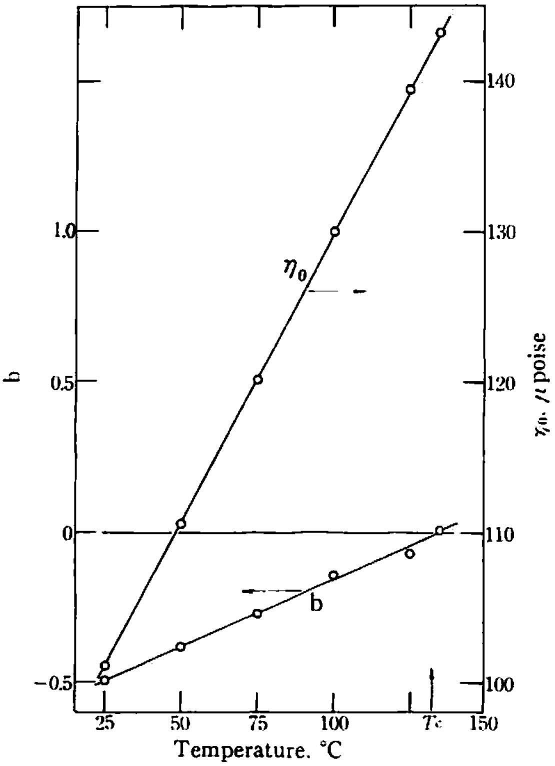

Fig. 5 Effect of temperature on η_0 and b in equation (5)

density as follows,

$$\eta=\eta_0+b\rho+c\rho^2+d\rho^3. \qquad (5)$$

The constants of equation (5), η_0, b, c and d, were evaluated using the measured values of viscosity at each temperature and were recorded in Table 4. These equations reproduce the measured values with a deviation not exceeding ±0.1%. The initial density dependency of the viscosity of ammonia, b, and the viscosity at zero density, η_0, were given against temperature in Fig. 5, respectively. From this figure it is known that the relation between the initial density dependency and temperature is linear and changes its sign from − to + at about the critical temperature and that the relation between the viscosity at zero density and temperature is also linear.

The data on ammonia given by other investigators are shown in Fig. 6. The data of Carmichael *et al.*¹⁾ by the rotating cylinder method, and of Iwasaki *et al.*²⁾ by oscillating disk method, show an effect of pressure on the viscosity of ammonia quite similar to the present measurements. Makita's data³⁾ by the rolling ball method and Stakelbeck's data⁴⁾ by the falling body method indicate a rapid increase in viscosity with an increase in pressure, in disagreement with the present measurements.

In Fig. 7 the relation between the viscosity of ammonia at 1 atm and temperature, including the data measured by the other investigators is given. Here, the measurements by Golubev *et al.*¹⁴⁾ were made using the capillary flow method. The discrepancies, not exceeding 1%, signify fairly good agreement, considering the differences in the methods of determination.

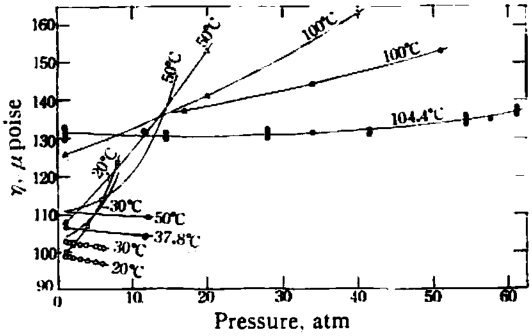

Fig. 6 Viscosity of ammonia given by several investigators
—○—: Iwasaki, Kestin and Nagashima²⁾
—●—: Carmichael *et al.*¹⁾
—□—: Stakelbeck⁴⁾
—△—: Makita³⁾
—◐—: Shimotake and Thodos⁵⁾

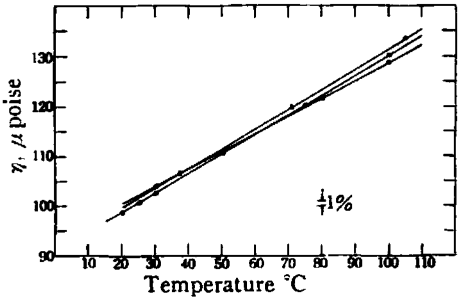

Fig. 7 Comparison of results for ammonia at 1 atm
—⊙—: Present results
—◐—: Iwasaki, Kestin and Nagashima²⁾
—△—: Carmichael *et al.*¹⁾
—●—: Golubev and Petrov¹⁴⁾

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14) I. F. Golubev, "Viscosity of Gases and Gaseous Mixtures", Fizmatgiz, Moscow, (1959)

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Nomenclature

T = period of oscillation

$2\pi\Delta$ = logorithmic decrement

T_0, Δ_0 = T, Δ *in vacuo*

$\tau = T/T_0$

η = viscosity

$\delta = \sqrt{\eta T_0/2\pi\rho}$ = boundary layer thickness

R = radius of disk

d = thickness of disk

D = total separation between plates

b_1 = upper separation

b_2 = lower separation

$b = \dfrac{2b_1b_2}{b_1+b_2}$ = the harmonic mean of the two separations, b_1 and b_2

I = moment of inertia of suspension

$\omega = 2\pi/T$

a = amplitude of oscillation

$\nu = \eta/\rho$

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