STUDIES ON THE *P-V-T* RELATIONS OF FLUIDS AT HIGH PRESSURE   I

The Compressibility of Ammonia

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Experimental

Method for gaseous ammonia

The measurements were made by the use of the constant volume type apparatus. The schematic diagram of the apparatus is shown in Fig. 1 and the cross-section of the high pressure gas pipet (A in Fig. 1) in Fig. 2.

The apparatus can be divided into two main parts. One is the high pressure system (steel-tubing side in Fig. 1) in which the *P-V-T* measurements for certain amounts of gaseous ammonia are made at
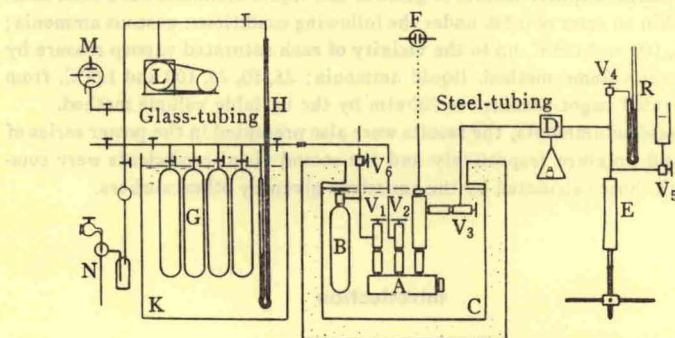

Fig. 1   Schematic diagram of apparatus for gaseous ammonia

A : High pressure gas pipet   B : Sample cylinder
C : Thermostat   D : Pressure balance
E : Oil injector   F : Pilot lamp
G : Glass cylinder   H : Mercury manometer
K : Thermostat   L : Vacuum pump
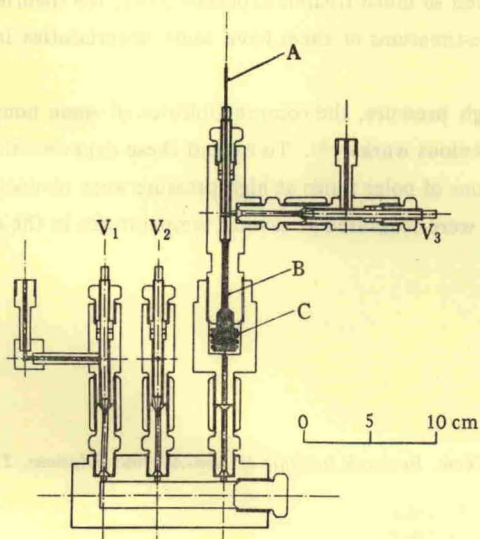M : Vacuum gage   N : Aspirator
R : Mercury manometer

Fig. 2   High pressure gas pipet
A : Insulated electrode
B : Mercury
C : Bellows
V : Valves

the desired conditions. Another is the low pressure system (glass-tubing side in Fig. 1) in which the molar quantities of ammonia employed above are determined from the measured values of *P*, *V* and *T* in the expanded state near to 1 atm.

The operations are as follows: After evacuating sufficiently the high pressure gas pipet (A), which has the known volume v, through the valve (V_2), (V_2) is closed and then the sample ammonia is introduced slowly from the sample cylinder (B) into the pipet up to some desired pressures. Simultaneously, the oil pressure in the steel-tubing is raised by handling the oil injector (E) and it is balanced with the pressure of ammonia in the pipet.

As shown in Fig. 2, the pipet has the stainless-steel bellows (C) filled with mercury (B), the capillary and the insulated electrode (A). The sample gas is separated from the pressure-transmitting oil by the bellows and mercury. If the pressure of the sample gas in the pipet is slightly higher than the oil pressure in the capillary, then the bellows is contracted with high sensitivity and the mercury is pushed up in the capillary to touch the lower end of the electrode. If the pressure of the sample gas is slightly lower than the oil pressure, the contact between the mercury and the electrode breaks off. This make-break of the contact takes place with very small pressure difference between both sides of the bellows. So the pressure balancing state can be detected very sharply by the use of the electronic circuit which was reported previously in detail[4].

When the pressure change of the sample gas in the pipet becomes too small to be detected, it is admitted that the temperature of the sample gas comes to equilibrium with the temperature of the oil thermostat (C). Then the pressure of the sample is measured by the use of the pressure balance (D) and the temperature of the sample is determined to be equal to the temperature of the thermostat which is measured by the mercury thermometer. After that, opening the valve (V_2) very slowly, the sample gas in the pipet is expanded into the low pressure system which was evacuated previously to one hundredth millimeter of mercury.

The low pressure system is composed of seven glass cylinders (G) having the known volume of about 300, 500 or 1,000 cm³ (total volume is about 7,000 cm³), the mercury manometer (H) and the connecting capillary having the inner diameter of 2 millimeters. It is set up in the water thermostat (K) kept constant at 25°C. The pressure of the expanded sample gas in the low pressure system is determined by the use of the cathetometer by measuring the height of mercury in the manometer (H).

By the operations mentioned above, the compressibility factor *Z* may be obtained as follows:

$$Z=\frac{Pv}{n\boldsymbol{R}T_1},$$

with $\quad P=P_1+P_2+\varDelta P,$

$$v=v_1+\varDelta v_1+\varDelta v_2,$$

$$n=\left(\frac{P_3}{\boldsymbol{R}}\right)\left(\frac{v_1+\varDelta v_1}{Z_1T_1}+\frac{Z_2T_2}{v_2}+\frac{v_3}{Z_3T_3}\right),$$

4) T. Toriumi, K. Date and H. Iwasaki, *Bull. Chem. Research Institute of Non-Aqueous Solutions, Tohoku Univ.*, **10**, 263 (1961)

where P : the absolute pressure of the sample [atm],

           P_1: the pressure reading of the pressure balance [atm],

           P_2: the atmospheric pressure [atm],

           P_3: the expanded sample gas pressure [atm],

           ΔP: the pressure difference between in- and out-side of the bellows [atm],

    T_1, T_2, T_3: the temperatures of the sample in the pipet, the glass cylinders and the connecting capillary, respectively [K],

    Z_1, Z_2, Z_3: the compressibility factors of the sample at pressure P_3 and at temperatures T_1, T_2 and T_3, respectively*,

           v_1: the inner volume of the pipet at 50°C and 1 atm [cm³],

           v_2: the volume of the glass cylinders and the gas phase in the left tube of the mercury manometer (H) [cm³],

           v_3: the volume of the connecting capillary [cm³],

           Δv_1: the change in volume of the pipet due to temperature change from 50°C to T_1 [cm³],

           Δv_2: the change in volume of the pipet due to pressure change from 1 atm to P [atm],

           n: moles of the sample gas,

           R: gas constant, 82.0567 ± 0.0034 [cm³·atm/mol·deg].

Precision on the measurement: The pressure P_1 was obtained by the measurement with the free-piston type pressure balance which was previously reported in detail[4].

The pressure balance was calibrated within the error of 0.02% by the use of the standard mercury manometer. The atmospheric pressure P_2 was obtained by the measurement with the Fortin type barometer to the accuracy of 0.1 mmHg.

The expanded gas pressure P_3 was obtained to measure the height of the mercury manometer (H) within the error of 0.05 mmHg by the use of the cathetometer of 1 meter long. The pressure-difference detector composed of mercury, bellows and electrode was found to be sensitive within a pressure-difference of 0.001 atm and to be reproducible within a pressure-difference of 0.01 atm by the test connecting two mercury manometers to the tubings both inside and outside of the bellows.

As shown in Fig. 2, the high pressure gas pipet is composed of 18–8 stainless-steel cylinder which has 40 cm³ of inner volume, two valves for in- and outlet of the sample and the pressure difference detector. The tips and the seats of the spindles of the valves were made of hardened tool steel, so that the volume change of the pipet would be negligibly small in the transformations of these parts.

The inner volume of the pipet v_1 was determined within an error of 0.10% by the operation as

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*   These values around 1 atm were estimated by the use of the experimental equations given in the previous paper[5] and used in this work.

5) K. Date and H. Iwasaki, *Annual Report of the Asahi Glass Foundation for the Contribution to Industrial Technology*, **11**, 65 (1965)

follows. The high pressure gas, of which the compressibility factor is accurately known, is introduced into the pipet. Then, its *P-V-T* relations are measured in the same operation on the measurement of the compressibility factor for ammonia gas. Thus the volume v_1 can be calculated using these data. In this work, it was determined at temperatures 50 and 100°C and pressures up to 100 atm using 99.99% pure nitrogen*. It resulted that Δv_2, the change in volume of the pipet with the pressure change from 1 atm, was negligibly small up to 100 atm. The values of Δv_1 (the change in volume of the pipet with the temperature change from 50°C) at 25, 75 and 125°C were determined to inter- and extrapolate the experimental values of Δv_1 at 50 and 100°C in regard to temperature.

The volume V_2 can be calibrated seperately to divide into three parts, namely, the volumes of glass cylinders, the volume of gas phase in the left leg of mercury manometer (H) and the volume of the connecting capillary. First, the volume of each glass cylinder was calibrated to measure the weight of the water which was filled in the cylinder at a constant temperature. They were determined for 300 ± 0.02 to $1,000\pm0.08$ cm³ respectively, that is, within an error of 0.01%. Second, the volume of gas phase in the left leg of the manometer (0 to 60 cm³) was calibrated in an error of ±0.01 cm³ to measure the weights of mercury filled in the leg on which the scale was marked. Last, some amount of nitrogen filled in any glass cylinder at known pressure and temperature was expanded into the connecting capillary which was evacuated previously, and its pressure change was measured. Then, the volume of the connecting capillary was determined for 14.50 ± 0.2 cm³ by the calculation to make use of their values of the pressure change, the temperature and the volume of the glass cylinder.

The temperatures of each thermostat and the connecting capillary, T_1, T_2 and T_3, respectively, were measured to 0.01°C by the mercury thermometers which were calibrated within the errors of 0.03°C in 0 to 50°C range, 0.04°C in 50 to 100°C range and 0.05°C in 100 to 150°C range at the National Research Laboratory of Metrology. Measuring the temperatures at several positions in both thermostats by the high sensitive thermistors, it was assured that their temperatures were constant and uniform within 0.01°C throughout this experimental work.

In the facts mentioned above, it is believed that the compressibility factors for gaseous ammonia would be obtained experimentally by this apparatus and operation within an error of 0.2% in maximum, calculating from the above errors which were accompanied with the experimental pressure, volume and temperature values.

Method for liquid ammonia

In the case of the measurement of the compressibility factor or the specific volume for liquid ammonia, the apparatus and method of the variable volume type are more suitable than the constant volume type. In this method, the compressibility factor or the specific volume for any liquid sample is determined to measure the pressure-volume relations for any known amount of the sampe at the

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* In our previous work[5], the comressibility factors of nitrogen were measured at 50 and 100°C and up to 100 atm by the variable volume method. It was shown that these values also agreed well with the values given by Michels[6,7]. They were then used for the calibration of the pipet volume in this work.

6) A. Michels, H. Wuoters and J. DeBoer, *Physica*, **1**, 587 (1934)

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

known constant temperature in principle. In this study, this method was then adopted and the piezo-meter shown in Fig. 3 was made for the measurement of *P-V-T* relations for liquid ammonia. As shown in Fig. 4, the whole apparatus is composed of the piezometer in the oil thermostat connected with the part for measuring the pressure of the sample (shown as steel-tubing side) and with that for measuring the amount of the ammonia sample (shown as glass-tubing side).
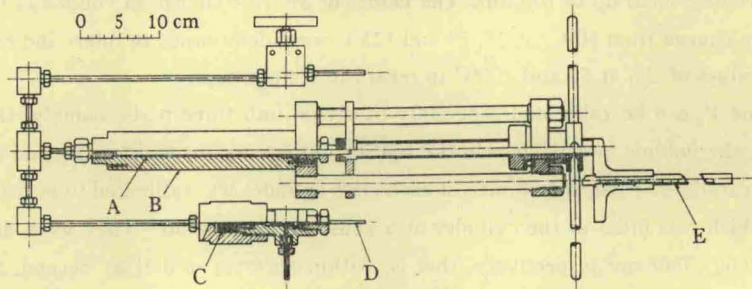

Fig. 3   Piezometer

A : Piston   B : Cylinder
C : Bellow and mercury   D : Electrode
E : Depth gage
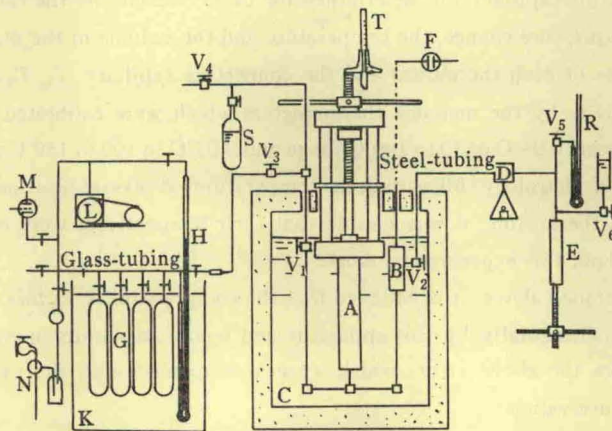
Fig. 4   Schematic diagram of apparatus for liquid ammonia

A : Piezometer   B : Pressure difference detector
C : Oil thermostat   D : Pressure balance
E : Oil injector   P : Pilot lamp
G : Glass cylinder   H : Mercury manometer
K : Water thermostat   L : Vacuum pump
M : Vacuum gage   N : Aspirator
R : Mercury manometer   S : Sample cylinder
T : Depth gage   V : Valves

The piezometer consists of the 18–8 stainless steel cylinder (B), the well polished and hardened tool steel piston (A) having the screw rod and handle movable by hand, the same pressure difference detector as that in the measurement for gaseous ammonia and some valves.

Teflon rings containing 30% glass-fiber by weights were used for packing between the piston and the cylinder and they were set so well that the inner volume change of the piezometer by the transformation of the packing would be negligibly small. The moving distance of the piston stroke (200 mm in maximum) was measured within an error of 0.02 mm by the depth gage fixed on the top of the screw rod. The inner volume of the piezometer from 15 to 35 cm^3 can be changed by moving the piston up or down to change its position against the cylinder. The relation between the inner volume of the piezometer and the positions of the piston was determined by the calibration described later. The parts of the apparatus for measuring both the pressure and the mass of the sample are the same as those for the gaseous ammonia mentioned in the previous section.

The operations are as follows: After sufficiently evacuating the inside of the piezometer, any desired amount of liquid ammonia sample is introduced into the piezometer by distillation. Then, the valve (V_1) is closed and the valve (V_2) is opened. The temperature of the oil thermostat is raised slowly from room temperature to the desired temperature, while the vapor pressure of the sample and the oil pressure in the tubing of the pressure measurement system are kept to be equal by handling the oil injector (E).

The temperature of the thermostat is kept constant at the desired value, then the piston is pushed very slowly into the cylinder and the sample is compressed. The volumes of the compressed liquid ammonia in any piston-positions can be obtained to read the readings of the depth gage.

The pressures of the sample are measured by the pressure balance (D) through the pressure difference detector at the same time. Finishing the compression process, the volume and the pressure relation in the expansion process is measured in the similar manner mentioned above by pulling the piston out. In these processes, it was assumed that the temperature of the sample reached in equilibrium with the temperature of the thermostat when the pressure of the sample became constant within the change of 0.01 atm.

Both measured values of the pressure at the same volume in the compression and the expansion processes always agreed well within 0.01 atm which was the experimental error in the pressure measurements. Finally, the sample is introduced into the low pressure system of glass and its amount is measured by the same operation as the measurement for gaseous ammonia.

Precision on the measurement: The volumes of the piezometer correlative with the piston stroke were determined at 50 and 100°C using 99.99% pure nitrogen by the same operation as for the constant volume method*.

The inter- and extrapolated values were used for the volumes at other temperatures. It resulted that they could be taken as the linear functions of the piston stroke within the error of 0.1% up to 500 atm. The errors for other measurement variables were the same as for the cases of gaseous ammonia. It is believed that the compressibility factor of liquid ammonia would be obtained experimentally by this apparatus and operation within the error of 0.2% in maximum, calculated from the above errors which were accompanied with the measured pressure, volume and temperature values.

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* For the compressibility factor of nitrogen at 50 and 100°C, the values by our previous work[5] were used for the pressure ranges up to 100 atm and the values by Michels[6,7] were used abuve 100 atm, respectively.

Purity of ammonia

Commercial ammonia was purified by repeated distillation and dehydrated by metallic sodium. It was used for the sample ammonia in this study. The amount of the innert gases in it was determined to be less than 0.04% by gas adsorbing analysis. It is believed that the sample is sufficiently more than 99.9% in purity.

Results and Discussions

Gaseous ammonia

The *P-V-T* relations of gaseous ammonia were measured at 25, 50, 75, 100 and 125°C up to the neighborhood of each saturated vapor pressure. The smoothed values of the compressibility factor of ammonia were obtained graphically from a lot of the experimental data. They are shown in Tables 1 and 2, *vs.* pressure and density respectively. All of the deviations between the experimental and smoothed values are less than 0.1%.

There are not so many experimental works for the *P-V-T* relations of gaseous ammonia reported by other workers. The data given by Meyers and Jessup[8] (−35 to 300°C, 85.5 to 1300 cc/g, 0.865 to 28.378 atm) and by Beattie and Laurence[9] (50 to 325°C, 20 to 95 cc/g, 14.37 to 130.40 atm) can be taken for the comparison with these results in the ranges of these experimental pressure and temperature conditions. And, also, the compressibility factor of gaseous ammonia had been measured preparatively in this laboratory in the ranges of 25 to 125°C and up to 45 atm by the variable volume method using the glass-piezometer and mercury-piston[5]. The data of this work were compared with the above three previous data.

They are shown in Table 3 in terms of the compressibility factor and the deviations from those of this work at each pressure and temperature. It is shown that the data given by Meyers and Beattie agree with those of this work with the deviations of about 0.2% through their almost whole ranges of the experimental conditions excepting with the deviations of 0.4 to 0.5% in the neighborhood of the saturated vapor pressures at 25 and 75°C, and that the data of our previous work are in fair agreement with those of this work at each pressure and temperature except in the neighborhood of the saturated vapor pressures at 50 and 75°C. The facts that the data of our previous work had considerablly smaller values than of this work and of Beattie and Laurence in the neighborhoods of the saturated vapor pressures at 50 and 75°C, can be understood as follows: the previous measurements were made by the method which was to measure optically or electrically the volume of sample ammonia compressed by mercury piston into the glass-piezometer. Approaching near to the saturated vapor pressures, it was afraid that the sample ammonia might be caught partly into the mercury becoming fine mists. Therefore, it is considered that the previous values were measured too small in these pressure ranges at 50 and 75°C.

8) C. H. Meyers and R. S. Jessup, *Refrig. Eng.*, **11**, 345 (1925)

9) J. A. Beattie and C. K. Laurence, *J. Am. Chem. Soc.*, **52**, 6 (1930)

It was tried to develop the experimental compressibility factor Z of gaseous ammonia in this work in the power series of density $1/V$ and pressure P respectively at each temperature. The results were obtained as shown in Table 4, from the calculation by the least squares method.

The Z values calculated by the use of the coefficients given in Table 4 agreed with the experimental Z values with the average deviation not exceeding 0.2% approximately up to the saturated vapor

Table 1   Compressibility factor of gaseous ammonia

P (atm)	$Z = Pv/nRT$				
	25°C	50°C	75°C	100°C	125°C
0	1.0000	1.0000	1.0000	1.0000	1.0000
2	0.9780	0.9856			
4	0.9546	0.9704			
5			0.9724	0.9787	0.9834
6	0.9308	0.9544			
7	0.9171				
8	0.9027	0.9372			
9	0.8862				
9.3	0.8800				
9.5	0.8743				
9.7	0.8656				
10		0.9188	0.9420	0.9560	0.9660
12		0.8993			
14		0.8793			
15			0.9089	0.9318	0.9477
16		0.8592			
18		0.8385			
19		0.8255			
19.5		0.8150			
19.8		0.8027			
20			0.8729	0.9061	0.9286
25			0.8340	0.8788	0.9086
30			0.7925	0.8502	0.8878
35			0.7435	0.8199	0.8662
40				0.7882	0.8437
45				0.7540	0.8204
50				0.7174	0.7962
55				0.6764	0.7712
60				0.6290	0.7446
65					0.7170
70					0.6873
75					0.6556
80					0.6205
85					0.5813
90					0.5350
95					0.4720

Table 2 Compressibility factor of gaseous ammonia

$1/V$ (mol/l)	$Z=Pv/nRT$				
	25°C	50°C	75°C	100°C	125°C
0	1.0000	1.0000	1.0000	1.0000	1.0000
0.2	0.9477	0.9595			
0.25			0.9599	0.9668	0.9725
0.4	0.8926	0.9195			
0.45	0.8715				
0.5	0.8130	0.8992	0.9203	0.9341	0.9453
0.6		0.8798			
0.7		0.8603			
0.75			0.8811	0.9017	0.9183
0.8		0.8393			
0.85		0.8275			
0.9		0.8140			
0.95		0.7946			
1		0.7545	0.8424	0.8698	0.8916
1.25			0.8042	0.8384	0.8651
1.5			0.7664	0.8073	0.8388
1.75			0.7202	0.7767	0.8128
2				0.7476	0.7880
2.25				0.7192	0.7643
2.5				0.6917	0.7412
2.75				0.6655	0.7191
3				0.6405	0.6975
3.5					0.6560
4					0.6158
4.5					0.5791
5					0.5446
5.5					0.5123
6					0.4812

pressures.

The coefficients B in Table 4 can be regarded as the experimental second virial coefficients. They were compared with the second virial coefficients given by Keyes[10] and the theoretically calculated ones with the assumption of some adequate potential function on the intermolecular force of ammonia.

B (cc/g) $= 2.4 - (2316/T) \exp (7.744 \times 10^4/T^2)$ for the second virial coefficient B of ammonia had been presented by Keyes. This is the experimental equation obtained by correlating the experimental P-V-T data of Meyers and Jessup with those of Beattie and Laurence. For the theoretical calculation of the second virial coefficient, it was assumed that the intermolecular force of ammonia might be represented by the Stockmayer potential function. The parameters in the function were taken as follows: $r_0=2.60\text{Å}$, $b_0=(2Nr_0^3/3)=22.12$ cc/mol, $\varepsilon/k=320$ K and $\mu=1.47$ debyes. Then, using the

10) F. G. Keyes, *J. Am. Chem. Soc.*, **60**, 1761 (1938)

Table 3   Comparison of compressibility factor for gaseous ammonia

P (atm)	Present work	Previous work[5]	Deviation (%)	Meyers et al.[8]	Deviation (%)	Beattie et al.[9]	Deviation (%)
				25°C			
2	0.9780	0.9780	0.00	0.9784	0.04		
4	0.9546	0.9546	0.00	0.9564	0.09		
6	0.9308	0.9308	0.00	0.9332	0.26		
7	0.9171	0.9171	0.00	0.9209	0.41		
8	0.9027	0.9027	0.00	0.9081	0.58		
9	0.8862	0.8862	0.00				
				50°C			
2	0.9856	0.9856	0.00	0.9848	−0.08		
4	0.9704	0.9704	0.00	0.9690	−0.14		
6	0.9544	0.9544	0.00	0.9528	−0.17		
8	0.9372	0.9372	0.00	0.9356	−0.17		
10	0.9188	0.9188	0.00	0.9179	−0.10		
12	0.8993	0.8993	0.00	0.8998	0.06		
14	0.8793	0.8787	−0.07	0.8805	0.13	0.8805	0.13
16	0.8592	0.8557	−0.41			0.8606	0.16
18	0.8385	0.8271	−1.35			0.8395	0.12
20	0.8255	0.8040	−2.60				
				75°C			
5	0.9724	0.9724	0.00			0.9706	−0.18
10	0.9420	0.9420	0.00			0.9399	−0.22
15	0.9089	0.9089	0.00			0.9068	−0.23
20	0.8729	0.8729	0.00			0.8718	−0.13
25	0.8340	0.8340	0.00			0.8339	−0.01
30	0.7925	0.7925	0.00			0.7921	−0.05
35	0.7435	0.7385	−0.67			0.7463	0.38

relations of $B=b_0 B^*(T^*, t^*)$, $T^*=kT/\varepsilon$, $t^*=(8)^{-1/2} \mu^{*2}$ and $\mu^*=\mu/(\varepsilon r_0^3)^{1/2}$, the second virial coefficients B at each temperature T were obtained by the use of the table of the reduced second virial coefficient B^* given by Hirschfelder et al.[11]. The results have been represented graphically in Fig. 5. It shows that the values by Keyes and the theoretically calculated values have the deviations of about 5 and 10% respectively from the values of this work at each temperature.

Liquid ammonia

The *P-V-T* relations of liquid ammonia were measured at 25, 50, 75, 100 and 125°C from each saturated vapor pressure to 500 atm. The smoothed values of the compressibility factor and of the

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11) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York (1954)

Table 3   (continued)

P (atm)	Present work	Previous work[5]	Deviation (%)	Meyers et al.[8]	Deviation (%)	Beattie et al.[9]	Deviation (%)
				100°C			
5	0.9787	0.9787	0.00	0.9769	−0.18	0.9768	−0.19
10	0.9560	0.9560	0.00	0.9538	−0.23	0.9534	−0.27
15	0.9318	0.9318	0.00	0.9296	−0.23	0.9294	−0.26
20	0.9061	0.9061	0.00	0.9045	−0.18	0.9041	−0.22
25	0.8788	0.8788	0.00			0.8777	−0.12
30	0.8502	0.8502	0.00			0.8502	0.00
35	0.8199	0.8199	0.00			0.8208	0.11
40	0.7882	0.7882	0.00			0.7895	0.16
45	0.7540					0.7557	0.23
50	0.7174					0.7190	0.23
55	0.6764					0.6776	0.18
60	0.6290						
				125°C			
5	0.9834	0.9834	0.00			0.9816	−0.18
10	0.9660	0.9660	0.00			0.9633	−0.28
15	0.9477	0.9477	0.00			0.9444	−0.35
20	0.9286	0.9286	0.00			0.9255	−0.33
25	0.9086	0.9086	0.00			0.9063	−0.25
30	0.8878	0.8878	0.00			0.8861	−0.19
35	0.8662	0.8662	0.00			0.8652	−0.11
40	0.8437	0.8437	0.00			0.8436	−0.01
45	0.8204	0.8204	0.00			0.8208	0.05
50	0.7962					0.7968	0.07
55	0.7712					0.7720	0.10
60	0.7446					0.7460	0.19
65	0.7170					0.7188	0.25
70	0.6873						
75	0.6556						
80	0.6205						
85	0.5813						
90	0.5350						
95	0.4720						

Deviation = $(Z_{other\ worker} - Z_{present\ work})/Z_{present\ work}$

specific volume were obtained graphically plotting a lot of the experimental data. They are shown in Tables 5 and 7, respectively.

All of the deviations between the experimental and the smoothed values are less than 0.1%. The saturated vapor pressures shown in these tables were measured to be constant within the maximum fluctuation of 0.05 atm at each temperature. Table 6 shows the comparison of the saturated vapor pressures given by this work, by Beattie and Laurence[9] and by International Critical Tables[12]. It

Table 4   Experimental virial coefficients of gaseous ammonia

$Z = 1 + B(1/V) + C(1/V)^2 + D(1/V)^3$							Deviation from exptl. values	
Temp. (°C)	B	C	D		Range of $1/V$		Average (%)	Maximum(%)
25	−0.2708	0.1272	−0.3396	0	to	0.45	0.15	0.24
50	−0.2172	0.0628	−0.0556	0	to	0.90	0.09	0.17
75	−0.1568	−0.00080	······	0	to	1.75	0.19	0.44
100	−0.1361	0.00521	······	0	to	3.00	0.10	0.33
125	−0.1150	0.004770	······	0	to	6.00	0.10	0.20

$1/V$; (mol/l)

$Z = 1 + B'P + C'P^2 + D'P^3 + E'P^4$							Deviation from exptl. values	
Temp.(°C)	$B' \cdot 10^3$	$C' \cdot 10^6$	$D' \cdot 10^6$	$E' \cdot 10^8$	Range of P		Average (%)	Maximum (%)
25	−10.84	74	−30.4	······	0 to	9.3	0.06	0.14
50	−7.477	−34.6	−2.90	······	0 to	19.0	0.09	0.14
75	−5.438	−32.4	−0.607	······	0 to	35	0.06	0.15
100	−4.403	−7.70	−0.358	······	0 to	60	0.12	0.29
125	−3.442	−14.21	0.1584	−0.2354	0 to	90	0.17	0.38

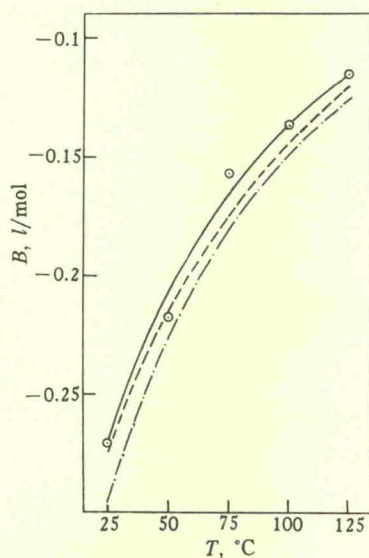P ; (atm)

Fig. 5   Second virial coefficient of ammonia
—⊙—: This work
———: Correlated   values   with Beattie   and   Meyer's   experimental data by Keyes
—·—·: Calculated   values   assuming Stockmeyer potential funtion

shows that they have agreed very nearly with one another at 25, 50 and 75°C but there have been slight differences to one another at 100 and 125°C.

Another experimental work has been reported only by Keyes[13] for the *P-V-T* relations of liquid

12) "International Critical Tables", **III**, 234, 235, McGraw-Hill, New York (1928)
13) F. G. Keyes. *J. Am. Chem. Soc.*, **53**, 965 (1931)

Table 5   Compressibility factor of liquid ammonia

P (atm)	25°C	50°C	Z=Pv/nRT 75°C	100°C	125°C
9.98	0.01156*				
20.05		0.02292*			
36.58			0.04223*		
50	0.05755	0.05672	0.05739		
61.65				0.07508*	
75	0.08600	0.08459	0.08522	0.09008	
98.15					0.1431*
100	0.1143	0.1122	0.1126	0.1176	0.1435
150	0.1702	0.1665	0.1661	0.1711	0.1866
200	0.2254	0.2200	0.2184	0.2222	0.2351
250	0.2800	0.2727	0.2695	0.2724	0.2832
300	0.3339	0.3246	0.3198	0.3213	0.3300
400	0.4398	0.4249	0.4179	0.4161	0.4209
500	0.5436	0.5246	0.5133	0.5082	0.5088

* These are at saturated vapor pressures.

Table 6   Comparison of saturated vapor pressure of ammonia

Temp. (°C)	Saturated vapor pressure (atm)		
	This work	Beattie et al.[9]	Int. Crit. Tables[12]
25	9.98	......	9.90
50	20.05	20.07	20.06
75	36.58	......	36.63
100	61.65	61.78	61.82
125	98.15	98.45	98.08

ammonia in these pressure and temperature ranges. In Table 7, the data by Keyes have been presented in terms of the specific volume at even pressures, to be compared with those of this work. Keyes had presented the smoothed PV values of ammonia in the ranges of 0 to 210°C and 100 to 1,100 atm in his report based on his experimental data.

It has been noted by him that his PV values were assured within an error of 0.25%. But they have some considerable irregularities, especially in the ranges of 0 to 30°C and 100 to 200 atm. Regarding this fact, it has been also pointed out by Davis[14], the reviewer, that there have been some unreasonable values in Keyes' data.

As shown in Table 7, Keyes' values are about 0.3 to 0.4% lower than those of this work at pressures of above 200 atm and at every temperature. Moreover, they are about 1% lower than those of this work at pressures of 100 atm and at temperatures of 50, 75 and 100°C.

In addition, the specific volumes of liquid ammonia at saturated vapor pressures have been obtained by extrapolating the experimental data down to the saturated vapor pressure at each tempera-

14) P. Davis, "Thermodynamic Functions of Gases", I, 66, Butterworths Sci. Publ., London (1956)

Table 7   Comparison of specific volume V (cc/mol) of liquid ammonia

P (atm)	25°C			50°C		
	Present work	Keyes	Deviation (%)	Present work	Keyes	Deviation (%)
9.98	28.34_2	28.25_0*	-0.32			
20.05				30.30_8	30.25_6*	0.17
50	28.16_3			30.08_2		
61.65						
75	28.05_7			29.90_7		
100	27.96_0	27.91	-0.17	29.74_2	29.46	-0.94
250	27.76_0			29.44_4		
200	27.57_5	27.65	0.29	29.17_1	29.01	-0.55
250	27.40_0			28.92_2		
300	27.22_8	27.15	-0.29	28.68_8	28.60	-0.31
400	26.90_2	26.93	-0.11	28.24_2	28.12	-0.42
500	26.60_0	26.67	-0.23	27.82_5	27.82	-0.00

* These are the values in International Critical Tables.

Deviation $=(V_{\text{Keyes}}-V_{\text{Present work}})/V_{\text{Present work}}$

Table 7   (continued)

P (atm)	75°C			100°C		
	Present work	Keyes	Deviation (%)	Present work	Keyes	Deviation (%)
36.58	32.98_6	32.98_8*	0.01			
50	32.79_3					
61.65				37.29_0	37.27_4*	-0.04
75	32.46_2			36.77_5		
100	32.16_2	31.83	-1.02	36.02_2	35.46	-1.55
150	31.63_5			34.92_0		
200	31.19_2	31.04	-0.48	34.02_5	34.01	-0.02
250	30.80_0			33.36_7		
300	30.45_0	30.37	-0.26	32.79_4	32.69	-0.30
400	29.84_5	29.77	-0.28	31.85_5	31.73	-0.37
500	29.33_0	29.25	-0.27	31.12_4	30.99	-0.41

ture. They have been represented in Table 7 together with the values given by International Critical Tables[12]. There have been little differences of 0.32 and 0.17% between both their values at 25 and 50°C respectively, but they have agreed well within the experimental error of this work at 75, 100 and 125°C.

The specific volumes of ammonia of this work have been represented graphically in Fig. 6 plotting them *vs.* temperature at even pressures. It is shown that they increase together with the increase of temperature and this tendency is more conspicuous with decreasing pressure.

Table 7   (continued)

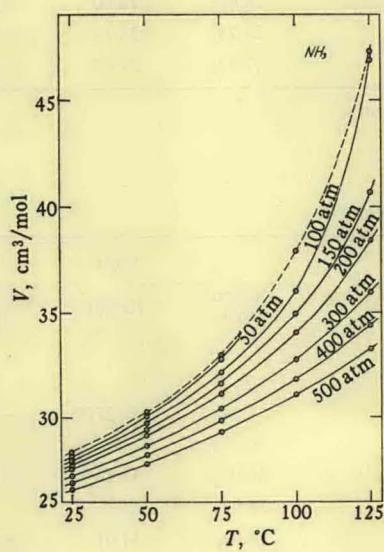| P (atm)	125°C		
	Present work	Keyes	Deviation (%)
98.15	47.62_0	47.65_4	0.07
100	46.88_0		
150	40.65_0		
200	38.40_0	38.23	−0.44
250	37.00_5		
300	35.94_0	35.78	−0.44
400	34.37_5	34.24	−0.40
500	33.24_5	33.14	−0.30

Fig. 6   Specific volume *vs.* temperature curves of liquid ammonia
—⊙—: Isobars above saturated vapor pressures
--⊙--: Saturated line

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