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STUDIES ON THE P - V - T RELATIONS OF FLUIDS AT HIGH PRESSURE IIIThe Compressibilities of Argon-Ammonia and Nitrogen-Ammonia
Gaseous Mixture Systems

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The measurements of the compressibility factors for three kinds of argon-ammonia gaseous mixtures and for three kinds of nitrogen-ammonia gaseous mixtures were made at 50°C and up to 50 atm within the experimental error of 0.2% by the constant volume method, respectively. The results were presented in tabular form of the compressibility factors at round pressures and densities. The results were also presented in the power series of density and pressure respectively, and their experimental second virial coefficients were compared with those calculated theoretically assuming the Lennard-Jones (12-6) and the Stockmayer potential functions to each intermolecular force pertinently. Both the experimental and the theoretical second virial coefficients were in agreement within the uncertainties inherent in the experimentals.

Introduction

There are few experimental works for the P - V - T relations of polar fluids and of the mixtures containing polar fluids. Therefore, the theories on their P - V - T relations have not been proved satisfactorily and the estimations of their P - V - T values have still some uncertainties at present.

To study the P - V - T relations of polar fluids at high pressure, the author had already measured the compressibility factors of gaseous and liquid ammonia in the range from 25 to 125°C and up to 500 atm¹⁾. In addition, the P - V - T values of ammonia in the neighborhood of the critical point had been measured and the critical values of ammonia had been determined from the above experimental P - V - T data²⁾. In this paper, for the study of the P - V - T relations of binary mixtures containing polar fluid, the compressibility factors of argon-ammonia mixtures and those of nitrogen-ammonia mixtures were measured at 50°C and up to 50 atm for three different compositions, respectively.

Other experimental works of the P - V - T relations for these binary mixtures, had been only reported by Kazarnowsky *et al.*³⁾ for a nitrogen-ammonia mixture from 150 to 300°C and up to 1640 atm. The data in this work could not be compared with their data because of the different experimental conditions of pressure and temperature.

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1) K. Date, *This Journal*, **43**, 1 (1973)

2) K. Date, *ibid.*, **43**, 17 (1973)

3) J. S. Kazarnowsky, G. B. Simonov and G. E. Aristov, *Zhur. fiz. Khim.*, **14**, 774 (1940)

Experimental

Method and apparatus

The constant volume type apparatus and method used to measure the values of P - V - T relations of the mixtures were the same as those for the gaseous ammonia in the previous work reported in detail¹⁾. It is believed that the compressibility factors of the mixtures would be obtained experimentally within the maximum error of 0.2% as well as for the gaseous ammonia in the previous work.

Materials

Both argon and nitrogen used were above 99.99% grade of purity, respectively. Commercial ammonia was purified by repeated distillation and dehydrated by metallic sodium. The ammonia obtained was sufficiently more than 99.9% of purity from the result of gas adsorbing analysis. The binary gas mixtures of the desired compositions were prepared in the storage vessels by mixing these gases. They were analyzed within the error of 0.1 mol% by the method of gas adsorption.

Results

Argon-ammonia system

The compressibility factors, $Z = PV/RT$, were measured at 50°C and up to 50 atm for three kinds of the binary mixtures of argon-ammonia as below :

91.8 mol% Ar— 8.2 mol% NH₃,

83.9 mol% Ar— 16.1 mol% NH₃.

63.5 mol% Ar— 36.5 mol% NH₃.

A large number of the experimental values of Z were plotted in a large graph against pressures or densities. The smoothed curves were drawn through each experimental point for each mixture. The values of Z read from the curves were in agreement with the experimental values within the deviation of 0.2%. These smoothed values of Z at round pressures and at round densities are shown in Table 1. In the table, the values of pure ammonia in the previous work¹⁾ and the values of pure argon in the previous work⁴⁾ were also represented.

The experimental equations of state were obtained to develop the experimental values of Z in the power series of density and pressure, respectively, by the use of the least square method. The results are shown in Table 2. The values of Z calculated by these equations were in agreement with the experimental values within the deviation of 0.2%.

4) K. Date, G. Kobuya and H. Iwasaki, *Bull. Chem. Res. Institute of Non-Aqueous Solutions, Tohoku Univ.*, 12, 33 (1963)

Studies on the P - V - T Relations of Fluids at High Pressure III

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Table 1 Compressibility factor of argon-ammonia system at 50°C

P , atm	$Z = PV/RT$				
	Composition, mol%				
	Ar 100.0 NH ₃ 0.0	Ar 91.8 NH ₃ 8.2	Ar 83.9 NH ₃ 16.1	Ar 63.5 NH ₃ 36.5	Ar 0.0 NH ₃ 100.0
0	1.0000	1.0000	1.0000	1.0000	1.0000
2	0.9992	0.9985	0.9981	0.9962	0.9856
4	0.9984	0.9973	0.9964	0.9925	0.9704
6	0.9975	0.9960	0.9947	0.9888	0.9544
8	0.9967	0.9949	0.9931	0.9852	0.9372
10	0.9960	0.9937	0.9916	0.9816	0.9188
12	0.9951	0.9925	0.9900	0.9780	0.8993
14	0.9943	0.9915	0.9885	0.9744	0.8793
16	0.9935	0.9904	0.9870	0.9708	0.8592
18	0.9928	0.9894	0.9855	0.9674	0.8385
20	0.9923	0.9883	0.9840	0.9640	
22	0.9915	0.9872	0.9826	0.9606	
24	0.9907	0.9863	0.9812	0.9572	
26	0.9900	0.9854	0.9800	0.9538	
28	0.9894	0.9845	0.9786	0.9505	
30	0.9888	0.9836	0.9773	0.9471	
40	0.9856	0.9798	0.9714		
50	0.9827	0.9767	0.9663		

Table 1 (continued)

$1/V$, mol/l	$Z = PV/RT$				
	Composition, mol%				
	Ar 100.0 NH ₃ 0.0	Ar 91.8 NH ₃ 8.2	Ar 83.9 NH ₃ 16.1	Ar 63.5 NH ₃ 36.5	Ar 0.0 NH ₃ 100.0
0	1.0000	1.0000	1.0000	1.0000	1.0000
0.2	0.9978	0.9967	0.9955	0.9903	0.9595
0.4	0.9957	0.9934	0.9913	0.9810	0.9195
0.6	0.9937	0.9905	0.9872	0.9719	0.8798
0.8	0.9917	0.9878	0.9835	0.9632	0.8393
1.0	0.9899	0.9853	0.9799	0.9548	
1.2	0.9881	0.9831	0.9766	0.9468	
1.4	0.9865	0.9810	0.9736		
1.6	0.9849	0.9792	0.9707		
1.8	0.9835	0.9776	0.9681		
2.0	0.9820	0.9763	0.9657		

Table 2 Experimental equations of state for argon-ammonia system at 50°C

Composition, mol%	$Z = 1 + B(1/V) + C(1/V)^2 + D(1/V)^3$			$1/V$, mol/l
	B	C	D	Range of $1/V$
Ar — NH ₃				
100.0 — 0.0	-0.01124	0.00113	—	up to 2.0
91.8 — 8.2	-0.01748	0.00282	—	up to 1.9
83.9 — 16.1	-0.02296	0.00291	—	up to 1.89
63.5 — 36.5	-0.04397	0.00420	—	up to 1.16
0.0 — 100.0	-0.2172	0.0628	-0.0566	up to 0.9
Composition, mol%	$Z = 1 + B'P + C'P^2 + D'P^3$			P , atm
	$B' \cdot 10^3$	$C' \cdot 10^6$	$D' \cdot 10^6$	Range of P
Ar — NH ₃				
100.0 — 0.0	-0.417	1.44	—	up to 50
91.8 — 8.2	-0.667	4.05	—	up to 49
83.9 — 16.1	-0.883	4.19	—	up to 48
63.5 — 36.5	-1.869	3.38	—	up to 29
0.0 — 100.0	-7.477	-34.6	-2.90	up to 19

Nitrogen-ammonia system

The compressibility factors were measured at 50°C and up to 50 atm for three kinds of the binary mixtures of nitrogen-ammonia as below :

87.3 mol% N₂—12.7 mol% NH₃,

77.0 mol% N₂—23.0 mol% NH₃,

62.3 mol% N₂—37.7 mol% NH₃.

The smoothed values of Z were obtained by the same method as in the case of the above argon-ammonia mixtures. They were in agreement with the experimental values within the deviation of 0.2%. They are shown in Table 3. In the table, the values of pure ammonia in the previous work¹⁾ and the values of pure nitrogen in the previous work⁵⁾ were also represented.

The experimental equations of state were obtained in the same manner as in the case of argon-ammonia systems. The results are shown in Table 4. The values of Z calculated by these equations were in agreement with the experimental values within the deviation of 0.2%.

Consideration on the second virial coefficients of the mixtures

The values of B in Tables 2 and 4 can be looked upon as the experimental second virial coefficients of the mixtures though they are not so accurate because they were obtained only from the experimental P - V - T data at higher pressures than several atmospheres.

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

Table 3 Compressibility factor of nitrogen-ammonia system at 50°C

P , atm	$Z = PV/RT$									
	Composition, mol%									
	N ₂ 100.0 NH ₃ 0.0	N ₂ 87.3 NH ₃ 12.7	N ₂ 77.0 NH ₃ 23.0	N ₂ 62.3 NH ₃ 37.7	N ₂ 0.0 NH ₃ 100.0					
0	1.0000	1.0000	1.0000	1.0000	1.0000					
2	1.0000	0.9994	0.9984	0.9965	0.9856					
4	0.9999	0.9988	0.9968	0.9930	0.9704					
6	1.0000	0.9982	0.9952	0.9896	0.9544					
8	1.0000	0.9976	0.9937	0.9865	0.9372					
10	1.0000	0.9971	0.9922	0.9834	0.9188					
12	1.0001	0.9965	0.9908	0.9805	0.8993					
14	1.0001	0.9960	0.9894	0.9777	0.8793					
16	1.0002	0.9955	0.9880	0.9751	0.8592					
18	1.0002	0.9950	0.9867	0.9725	0.8385					
20	1.0004	0.9944	0.9854	0.9701						
22	1.0005	0.9940	0.9842							
24	1.0006	0.9935	0.9830							
26	1.0007	0.9931	0.9818							
28	1.0010	0.9926	0.9807							
30	1.0012	0.9922	0.9796							
40	1.0023	0.9903								
50	1.0038	0.9886								

Table 3 (continued)

$1/V$, mol/l	$Z = PV/RT$									
	Composition, mol%									
	N ₂ 100.0 NH ₃ 0.0	N ₂ 87.3 NH ₃ 12.7	N ₂ 77.0 NH ₃ 23.0	N ₂ 62.3 NH ₃ 37.7	N ₂ 0.0 NH ₃ 100.0					
0	1.0000	1.0000	1.0000	1.0000	1.0000					
0.2	0.9999	0.9984	0.9958	0.9909	0.9595					
0.4	1.0000	0.9969	0.9919	0.9828	0.9195					
0.6	1.0003	0.9955	0.9882	0.9757	0.8798					
0.8	1.0005	0.9941	0.9849	0.9696	0.8393					
1.0	1.0009	0.9929	0.9818							
1.2	1.0015	0.9918								
1.4	1.0021	0.9907								
1.6	1.0028	0.9898								
1.8	1.0036	0.9889								
2.0	1.0045									

Table 4 Experimental equations of state for nitrogen-ammonia system at 50°C

Composition, mol%	$Z = 1 + B(1/V) + C(1/V)^2 + D(1/V)^3$			$1/V$, mol/l
N ₂ — NH ₃	B	C	D	Range of $1/V$
100.0 — 0.0	-0.00037	0.00131	—	up to 3.0
87.3 — 12.7	-0.0082	0.00114	—	up to 1.8
77.0 — 23.0	-0.0219	0.0034	—	up to 1.07
62.3 — 37.7	-0.0479	0.0123	—	up to 0.7
0.0 — 100.0	-0.2172	0.0628	-0.0566	up to 0.9

Composition, mol%	$Z = 1 + B'P + C'P^2 + D'P^3$			P , atm
N ₂ — NH ₃	$B' \cdot 10^3$	$C' \cdot 10^6$	$D' \cdot 10^6$	Range of P
100.0 — 0.0	-0.022	1.98	—	up to 100
87.3 — 12.7	-0.038	1.6	—	up to 48
77.0 — 23.0	-0.829	5.0	—	up to 28
62.3 — 37.7	-1.828	16.8	—	up to 18
0.0 — 100.0	-7.477	-34.6	-2.90	up to 19

They were compared with the values calculated theoretically as follows. The Lennard-Jones (12-6) potential function,

$$\varphi(r) = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6], \quad (1)$$

was adopted on the intermolecular forces between argon and argon, argon and ammonia, nitrogen and nitrogen, and nitrogen and ammonia. The Stockmayer potential function,

$$\varphi(r, \theta_1, \theta_2, \phi_2 - \phi_1) = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6] - (\mu^2/r^3) g(\theta_1, \theta_2, \phi_2 - \phi_1), \quad (2)$$

was adopted on the intermolecular forces between ammonia and ammonia. The figures of the parameters in the functions were given by Hirschfelder *et al.*⁶⁾ as below :

	$r_0(\text{\AA})$	$b_0 = (2/3)Nr_0^3$ (cc/mol)	ϵ/k (K)	μ (debyes)
Ar — Ar	3.405	49.80	119.8	—
Ar — NH ₃	3.002	34.14	195.8	—
N ₂ — N ₂	3.698	63.78	95.05	—
N ₂ — NH ₃	3.126	38.54	190.5	—
NH ₃ — NH ₃	2.60	22.12	320	1.47

where the force constants between a polar (subscript p) and a non-polar molecule (subscript n) were obtained from the empirical combination laws represented by the following equations :

$$(r_0)_{np} = (1/2) [(r_0)_n + (r_0)_p] \epsilon^{-1/6} \quad (3)$$

$$\epsilon_{np} = (\epsilon_n \epsilon_p)^{1/2} \epsilon^2 \quad (4)$$

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

The factor ξ is given by :

$$\xi = 1 + (1/4)[\alpha_n \mu_p^* / (r_c)_n^3] (\epsilon_p / \epsilon_n)^{1/2}, \quad (5)$$

in which α_n is the polarizability of the non-polar molecule ($\alpha_n = 1.76 \text{ \AA}^3$ for nitrogen and $0 \text{ \AA}^3$ for argon) and $\mu_p^* = \mu_p / [\epsilon_p (r_c)_p^3]^{1/2}$.

The numerical tables of the reduced second virial coefficient B^* had been given in the literature⁶⁾ for each potential function by :

$$B(T) = b, \quad B^*(T^*), \quad \text{for the Lennard-Jones (12-6) potential ;}$$

$$B(T) = b, \quad B^*(T^*, t^*), \quad \text{for the Stockmayer potential ;}$$

where $T^* = kT/\epsilon$ and $t^* = 8^{1/2} \mu_p^*$.

The theoretical values of the second virial coefficients for each pure gas were obtained by the use of the above values of the force constants and the tables of B^* . For the mixtures, they were obtained by the use of the following relation :

$$B_{mix} = x_n^2 B_n + 2x_n x_p B_{np} + x_p^2 B_p \quad (6)$$

where B_{mix} is the second virial coefficient for the mixture, B_n and B_p are the second virial coefficients calculated for each pure component of non-polar or polar molecule, B_{np} is the second virial coefficient in regard to the interaction between non-polar and polar molecules, and x_n and x_p are the mole fractions of non-polar and polar components in the mixture, respectively.

The results for the comparison are shown in Table 5 and graphically in Fig. 1. There exist the differences between the experimental and the values calculated theoretically for these binary systems from 0.05 to 9.9 cc/mol. However, it was estimated that these values of B_{exp} for the gradients of the isotherms at zero pressure had some uncertainties of which the quantities would be the same order as the above differences. From this viewpoint, it can be said that both the experimental and the calculated values of the second virial coefficients were in agreement with each other for these binary systems.

Table 5 Comparison of second virial coefficient for argon-ammonia and nitrogen-ammonia mixture systems at 50°C

Composition, mol%	B , cc/mol		Difference $B_{exp} - B_{calc}$, cc/mol
	Experimental B_{exp}	Calculated B_{calc}	
100% Ar	- 11.24	- 11.19	0.05
100% N ₂	- 0.37	- 0.27	0.10
100% NH ₃	- 217.2	- 207.3	9.9
91.8% Ar — 8.2% NH ₃	- 17.48	- 16.13	1.35
83.9% Ar — 16.1% NH ₃	- 22.96	- 22.33	0.63
63.5% Ar — 36.5% NH ₃	- 43.97	- 47.67	- 3.70
87.3% N ₂ — 12.7% NH ₃	- 8.20	- 11.48	- 3.28
77.0% N ₂ — 23.0% NH ₃	- 21.9	- 23.79	- 1.9
62.3% N ₂ — 37.7% NH ₃	- 47.9	- 46.35	1.5

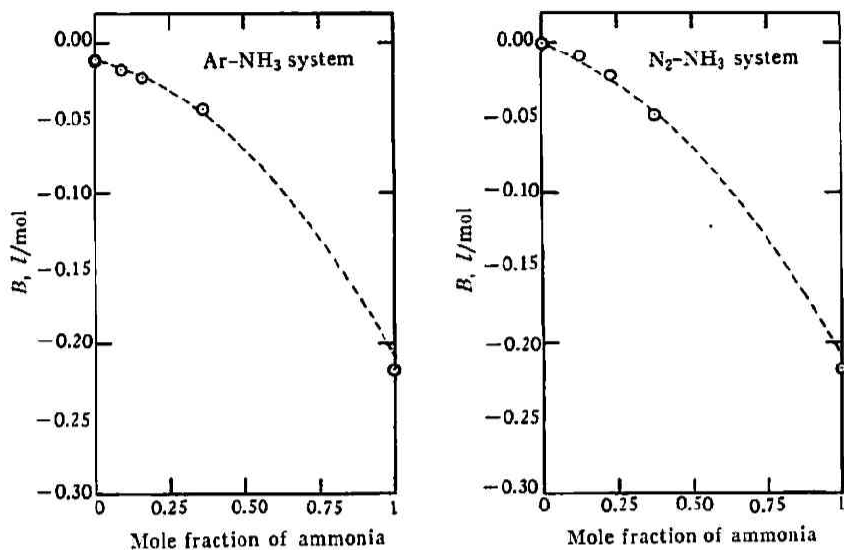


Fig. 1 Second virial coefficients of argon-ammonia and nitrogen-ammonia binary mixture systems both at 50°C

○: Experimental ----: Calculated

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