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

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By Kaoru Date

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Using the variable volume method, the $P–V–T$ relations of ammonia in the neighborhood of critical point have been measured within an error of 0.2% in regard to the compressibility factor Z. Seven $P–V$ isotherms were obtained in the range of 131.05 to 133.96°C, 109.33 to 117.05 atm and 53.42 to 110.22 cc/mol around the critical point.

The critical values of ammonia were determined from the isotherms as T_c $=132.3°C$, $P_c =111.7$ atm and $V_c =72.05$ cc/mol.

Introduction

For the experimental study of the *P-V-T* relation of polar fluid, the author had already measured the *P-V-T* relation of ammonia in gaseous and liquid states at several temperatures from 25 to 125°C and at pressures up to 500 atm and reported in the previous paper[1]. The experimental results for the *P-V-T* relation of ammonia were also reported in several papers by the other investigators, but there has been none in the neighborhood of its critical point. Therefore, the measurements of the *P-V-T* relation of ammonia were undertaken at several temperatures and in the pressure range from 108 to 117 atm around the critical temperature and pressure. In addition, the critical values of ammonia were determined by the use of these experimental *P-V-T* results.

Experimental

The method and apparatus were the same as those in the measurement of the *P-V-T* relation of liquid ammonia based on the variable volume type described in detail[1] in the previous paper. It was used for the sample ammonia that was prepared in the same manner as that in the previous work[1] and that was believed to be above 99.9% pure. The errors for every measurement variables were 0.01% for pressure P (110±0.01 atm), 0.1% for volume v (15±0.01 to 35±0.015 cc), 0.01% for temperature T (400±0.05 K) and 0.05% for mole n (0.3±0.00015 mol) respectively, similar to those in

the previous work[1]. Then it is believed that the compressibility factors of ammonia, $Z = Pv/n\boldsymbol{R}T$, were obtained within an error of 0.2% in maximum, estimating from the above errors for P, v, T and n.

Results on *P-V-T* measurement

The specific volumes of ammonia, V, were measured in the range from 53 to 110 cc/mol at each corresponding pressure and at seven constant temperatures in the range of 131.05 to 133.96°C. The results are presented in Table 1 and represented graphically in Fig. 1. It is shown in Fig. 1 that each smoothed isotherm is in excellent agreement with each experimental point. Each experimental pressure at each horizontal part of the isotherm from 131.05 to 132.25°C, that is, the saturated vapor pressure, was measured to be constant respectively at each constant temperature, within a maximum fluctuation of 0.06 atm.
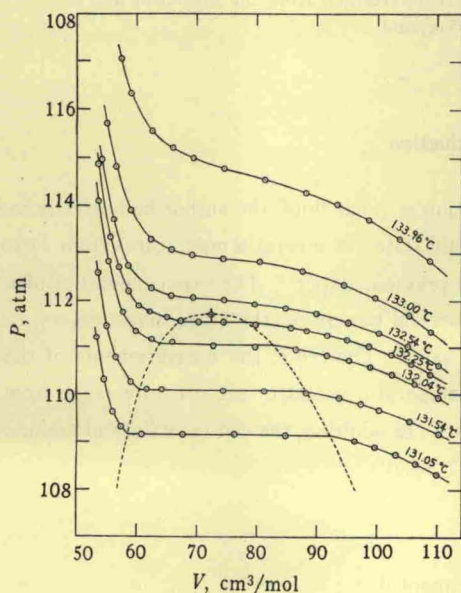
Fig. 1   Isotherms of ammonia in the neigh-
borhood of critical point

The broken line in Fig. 1 is the line obtained to connect the points of the specific volume of saturated vapor with those of saturated liquid on the isotherms. The point represented as ϕ is the critical point of ammonia determined in the following section.

Determination of critical values

There are several kinds of methods for the measurement of the critical values of any substances, that is, the critical temperature T_c, the critical pressure P_c and the critical specific volume V_c or the

Table 1   Experimental *P–V–T* values of ammonia
in the neighborhood of critical point

T (°C)	$1/V$ (mol/l)	P (atm)	V (cc/mol)	Z
131.05°C	9.110	108.33	109.77	0.3585
	9.396	108.55	106.43	0.3483
	9.709	108.75	103.00	0.3377
	10.042	108.89	99.58	0.3269
	10.399	109.03	96.16	0.3161
	11.784	109.14	84.86	
	13.114	109.17	76.25	
	13.114	109.17	67.71	
	14.768	109.17	60.85	
	17.420	109.31	57.41	0.1892
	17.843	109.65	56.04	0.1852
	18.297	110.32	54.65	0.1818
	18.720	111.21	53.42	0.1791
131.54°C	9.073	109.18	110.21	0.3623
	9.485	109.44	105.43	0.3474
	9.971	109.68	100.29	0.3312
	10.286	109.81	97.22	0.3215
	10.664	109.93	93.77	0.3104
	11.350	110.03	88.11	
	12.308	110.07	81.25	
	13.444	110.09	74.38	
	15.603	110.13	64.09	
	16.208	110.12	61.70	
	16.963	110.27	58.95	0.1957
	17.685	110.80	56.55	0.1887
	18.127	111.45	55.17	0.1852
	18.657	112.56	53.60	0.1817
132.04°C	9.075	109.93	110.19	0.3643
	9.406	110.23	106.32	0.3525
	9.753	110.44	102.53	0.3406
	10.110	110.59	98.91	0.3290
	10.474	110.73	95.47	0.3180
	10.903	110.84	91.72	0.3508
	11.552	110.95	86.57	0.2889
	12.547	111.00	79.70	
	13.730	111.04	72.83	
	15.163	111.12	65.95	
	15.985	111.17	62.56	0.2092
	16.678	111.35	59.96	0.2008
	17.319	111.75	57.74	0.1940
	18.064	112.82	55.36	0.1878
	18.648	114.10	53.63	0.1840

132.25°C	9.190	110.44	108.81	0.3612
	9.456	110.65	105.75	0.3518
	9.770	110.86	102.35	0.3411
	10.141	111.03	98.61	0.3291
	10.528	111.17	94.98	0.3174
	10.902	111.26	91.73	0.3068
	11.324	111.35	88.31	0.2956
	11.654	111.43	85.81	0.2874
	12.519	111.48	79.88	0.2677
	13.409	111.54	74.58	
	14.228	111.55	70.28	
	14.843	111.56	67.37	
	15.392	111.64	64.97	0.2180
	16.075	111.76	62.21	0.2090
	16.578	111.89	60.32	0.2029
	17.015	112.20	58.77	0.1982
	17.534	112.69	57.03	0.1932
	17.965	113.34	55.65	0.1896
	18.654	114.86	53.61	0.1851
132.54°C	9.073	110.60	110.22	0.3662
	9.517	111.02	105.08	0.3504
	9.972	111.31	100.28	0.3353
	10.509	111.53	95.16	0.3188
	11.112	111.72	89.99	0.3020
	11.785	111.83	84.85	0.2850
	12.547	111.92	79.70	0.2680
	13.412	112.04	74.56	0.2509
	14.409	112.08	69.40	0.2336
	15.198	112.12	65.80	0.2216
	16.032	112.26	62.38	0.2104
	17.062	112.73	58.61	0.1985
	17.790	113.70	56.21	0.1920
	18.420	114.96	54.29	0.1875
133.00°C	9.184	111.34	108.89	0.3638
	9.485	111.66	105.43	0.3532
	10.040	112.06	99.60	0.3349
	10.586	112.33	94.46	0.3184
	11.417	112.62	87.59	0.2960
	12.412	112.82	80.57	9.2727
	13.443	112.86	74.39	0.2519
	14.443	112.97	69.23	0.2347
	15.194	113.07	65.82	0.2233
	16.027	113.29	62.39	0.2121
	16.967	113.90	58.94	0.2014
	17.688	114.82	56.54	0.1948
	18.125	115.72	55.17	0.1916

133.96°C	9.196	112.83	108.74	0.3673
	9.642	113.30	103.71	0.3517
	10.143	113.70	98.59	0.3355
	10.704	114.03	93.42	0.3189
	11.329	114.28	88.27	0.3020
	12.281	114.55	81.43	0.2792
	13.410	114.78	74.57	0.2562
	14.410	114.99	69.40	0.2389
	15.158	115.21	65.97	0.2275
	15.989	115.56	62.54	0.2163
	16.917	116.33	59.11	0.2058
	17.419	117.05	57.41	0.2012

critical density $1/V_c$. Among the methods, there is one using the *P-V-T* relations in the neighborhood of the critical point.

Since the critical point can be defined as the position at which $(dP/dV)_T=0$ and $(d^2P/dV^2)_T=0$ at $T=T_c$, the determination of the critical values of ammonia was tried by the use of the above definition and the experimental *P-V-T* values in this work, as follows.

For T_c, the minimum values of $(dP/dV)_T$ at each isotherm, $(dP/dV)_{T, min}$, were estimated graphically and they were plotted against T as shown in Fig. 2. The T_c value was obtained as 132.33 ± 0.05°C extrapolating the line in Fig. 2 to $(dP/dV)_{T, min}=0$. As shown in Fig. 3, the P_c value was also obtained as 111.65 ± 0.05 atm in a similar manner as above for T_c. Nevertheless, the V_c value could not be obtained so clearly by the use of the extrapolation of $(dP/dV)_{T, min}$ to 0 in the graph of $(dP/dV)_{T, min}$ *vs.* V, in a similar manner as above for T_c and P_c, that it lay in the range of about 70 to 75 cc/mol.
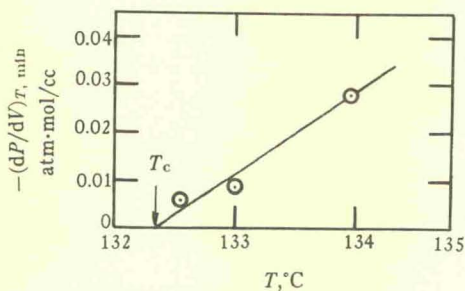

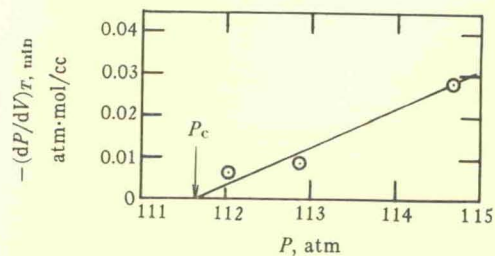Fig. 2 $(dP/dV)_{T, min}$ *vs.* temperature curve

Fig. 3 $(dP/dV)_{T, min}$ *vs.* pressure curve

On the other hand, there had been presented the method to determine the value of V_c very accurately by the use of the law of rectilinear diameters proposed by Cailletet and Mathias. This law claims that the arithmetical mean of the saturated liquid density $1/V_1$ and the saturated vapor density $1/V_g$ both at the same temperature, $(1/2)[(1/V_1)+(1/V_g)]_T$, decrease linearly to the critical point with the increase of temperature. It is only empirical but it has been confirmed since olden times that the law is applicable to many substances. According to this law, the value of $1/V_c$ can be easily deter-

mined as the value of $1/V$ at the point of intersection of two curves, that is, one is the straight line of $(1/2)[(1/V_1)+(1/V_g)]$ and the other is the curve connecting $1/V_1$ and $1/V_g$ lines smoothly, in the graph of $1/V$ vs. T. Using this method and the experimental values of density given in Table 2, the critical value was finally determined as $1/V_c=13.88\pm0.03\,mol/l=0.2364\pm0.0005\,g/cc$ or $V_c=72.05\pm0.08\,cc/mol$. It is also shown in Fig. 4.
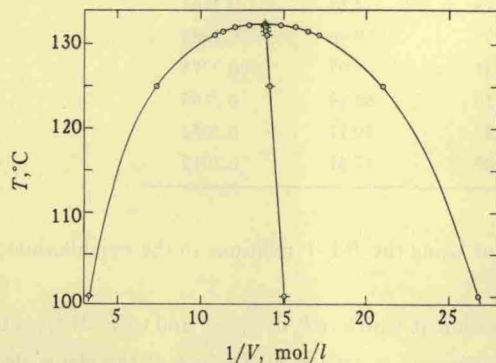
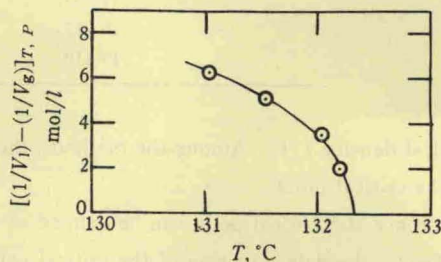Fig. 4   Law of rectilinear diameters for ammonia

Fig. 5 $[(1/V_1)-(1/V_g)]_{T,P}$ vs. temperature curve

Table 2   Experimental values of saturated vapor pressure, saturated vapor density and saturated liquid density of ammonia

Temp. t (°C)	Saturated vapor pressure, P (atm)	Saturated vapor density, $1/V_g$ (mol/l)	Saturated liquid density, $1/V_1$ (mol/l)
100	61.65*	3.30**	26.81*
125	98.15*	7.34**	21.00*
131.05	109.16	10.84	17.15
131.54	110.09	11.32	16.47
132.04	111.06	12.08	15.71
132.25	111.55	12.81	14.84

* These are the experimental values in previous work[1].
** These are the extrapolated values of the experimental densities of gaseous ammonia in previous work[1] to the saturated vapor pressures.

To prove the validity for the values of T_c and P_c obtained above, an examination was done as follows.
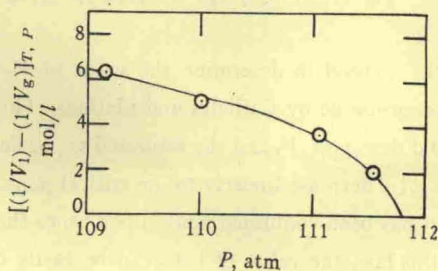
Fig. 6 $[(1/V_1)-(1/V_g)]_{T,P}$ vs. pressure curve

Since it is expected that the limit values of $1/V_1$ and $1/V_g$ to the critical point are to be equal, the experimental $[(1/V_1)-(1/V_g)]_{T, P}$ values were plotted against T or P in graph and the curve was extrapolated through the experimental points to zero. Then the value of T or P at $[(1/V_1)-(1/V_g)]_{T, P}$ $=0$ was obtained as 132.38°C or 111.84 atm respectively which corresponded very nearly to the value of T_c or P_c mentioned above. These figures are shown in Fig. 5 and 6.

Finally, for the most probable critical values of ammonia, they were determined as $T_c=132.3$°C, $P_c=111.7$ atm, $V_c=72.0_5$ cc/mol or $1/V_c=0.236_4$ g/cc and the critical compressibility factor $Z_c=P_cV_c/$ $RT_c=0.242_0$, respectively in this work.

Table 3   Comparison of critical constants of ammonia

Year	T_c (°C)	P_c (atm)	$1/V_c$ (g/cc)	Method*	Investigators
1884	130.0	115.0		?	J. Dewar
1886	131.0	113.0		(1)	C. Vincent *et al.*
1903	132.53			(1)	M. Centnerswer
1904			0.239	(2)	E. Mathias
1908	132.3			(1)	Jacqerod
1910	132.1	111.3		(1)	F. Scheffer
1912	132.9	112.3		(1)	E. Cardoso *et al.*
1913	132.3			(1)	Estreier *et al.*
1918	132.3		0.2364	(1, 2)	A. Berthoud
1918	132.3		0 2362	(1, 2)	A. Berthoud
1920	132.35	111.3		(1)	Postma
1923			0.234	(2)	Cregoe *et al.*
Values selected	132.3	111.3	0.235	....	K. Kobe *et at.*
This work	132.3	111.7	0.2364	(2. 3)	

* (1) Disappearance of the meniscus

  (2) Law of rectilinear diameters

  (3) Pressure-volume-temperature relations; $(dP/dV)_{T, min}=0$

Kobe *et al.*[2] had presented the most probable critical values for many substances based on the experimental values by various workers and methods. The critical values of ammonia measured by other investigators and recommended by Kobe *et al.* are presented in Table 3 together with the values determined in this work for comparison.

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2) K. A. Kobe and R. E. Lynn, Jr., *Chem. Rev.*, **52**, 117 (1953)

THE TRANSFERENCE NUMBERS OF KCL AQUEOUS SOLUTION UNDER PRESSURE

BY YASUHIKO MATSUBARA, KIYOSHI SHIMIZU* AND JIRO OSUGI

The transference numbers of K^+ ion in KCl aqueous solutions have been determined at high pressure up to $1,500 \, kg/cm^2$ at the concentration from 0.01 to 0.1 N at 25°C and at 0.02 N at 15 and 40°C by the moving boundary method. The movement of the boundary was detected by the resistance measurement. Cadmium chloride was used as an indicator solution. The transference numbers at infinite dilution at 25°C were calculated by the empirical equation of Longsworth. The K^+ ion transference numbers decrease with the increase in pressure in all cases. This decreasing tendency becomes weaker with the increase in temperature. Besides, the K^+ ion transference number increases slightly with the increase in temperature at $1500 \, kg/cm^2$, while it decreases with the increase in temperature at atmospheric pressure. The ion-water interaction of K^+ ion is mostly dominated by the electrostriction, while the ion-water interaction of Cl^- ion involves the hydrogen bond additionally. It is considered that the hydrogen bond in the hydration shell of Cl^- ion is broken with the increase in pressure and/or temperature as that in pure water. That is to say, the hydration of Cl^- ion decreases to a small degree with the increase in pressure and/or temperature.

Introduction

Accurate data on the limiting equivalent conductances $\Lambda^°$ of electrolytes at infinite dilution give valuable information for the understanding of ion-solvent interaction. From this point of view, in our laboratory, the effects of temperature and pressure on the electrical conductances of electrolytes in aqueous solutions have been studied. When we want to discuss the cation- and anion-water interactions, we need to know the ionic transference numbers of electrolytes. Unfortunately, in spite of numerous accurate measurements of the conductances of aqueous solutions under high pressure, only a few measurements of the transference numbers were reported[1~4]. Then, the transference numbers of K^+ ion in KCl aqueous solutions were determined precisely under high pressures up to $1,500 \, kg/cm^2$. From the data obtained, the pressure and temperature effects on the transport processes of K^+ and Cl^- ions and, especially, on their ion-water interactions are discussed in this paper.

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1) F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **59**, 278 (1955)
2) F. T. Wall and J. B. Berkowitz, *ibid.*, **62**, 87 (1958)
3) R. L. Kay, K. S. Pribadi and B. Watson, *ibid.*, **74**, 2724 (1970)
4) G. J. Hills, P. J. Ovenden and D. R. Whitehouse, *Discussions Faraday Soc.*, **39**, 207 (1965)