

Since it is expected that the limit values of  $1/V_l$  and  $1/V_g$  to the critical point are to be equal, the experimental  $[(1/V_l)-(1/V_g)]_{T,P}$  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  $[(1/V_l)-(1/V_g)]_{T,P}=0$  was obtained as  $132.38^\circ\text{C}$  or  $111.84\text{ atm}$  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  $T_c=132.3^\circ\text{C}$ ,  $P_c=111.7\text{ atm}$ ,  $V_c=72.0_5\text{ cc/mol}$  or  $1/V_c=0.236_4\text{ g/cc}$  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	$T_c$ ( $^\circ\text{C}$ )	$P_c$ (atm)	$1/V_c$ (g/cc)	Method*	Investigators
1884	130.0	115.0		?	J. Dewar
1886	131.0	113.0		(1)	C. Vincent <i>et al.</i>
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 <i>et al.</i>
1913	132.3			(1)	Estreier <i>et al.</i>
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 <i>et al.</i>
Values selected	132.3	111.3	0.235	.....	K. Kobe <i>et al.</i>
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;  $(dP/dV)_{T, \text{min}}=0$

Kobe *et al.*<sup>2)</sup> 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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## THE TRANSFERENCE NUMBERS OF KCl AQUEOUS SOLUTION UNDER PRESSURE

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The transference numbers of  $K^+$  ion in KCl aqueous solutions have been determined at high pressure up to 1,500 kg/cm<sup>2</sup> 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 Longworth. 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<sup>2</sup>, 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  $\Lambda^\circ$  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<sup>1-4</sup>). Then, the transference numbers of  $K^+$  ion in KCl aqueous solutions were determined precisely under high pressures up to 1,500 kg/cm<sup>2</sup>. 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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