

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  $132.33 \pm 0.05^\circ\text{C}$  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  $111.65 \pm 0.05$  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.

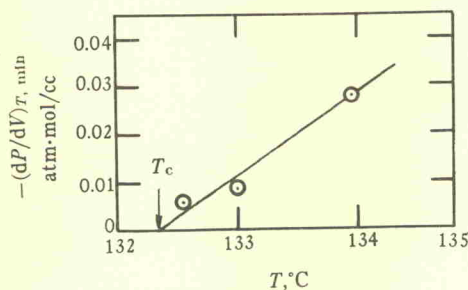


Fig. 2  $(dP/dV)_{T, \min}$  vs. temperature curve

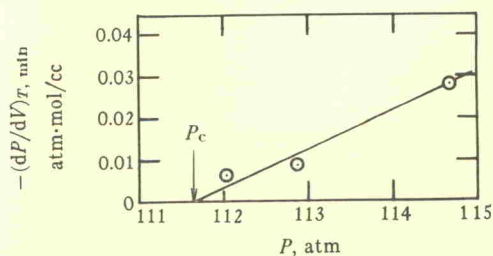


Fig. 3  $(dP/dV)_{T, \min}$  vs. pressure curve

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  $1/V_l$  and the saturated vapor density  $1/V_g$  both at the same temperature,  $(1/2)[(1/V_l) + (1/V_g)]_T$ , 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  $(1/2)[(1/V_l) + (1/V_g)]$  and the other is the curve connecting  $1/V_l$  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  $1/V_c = 13.88 \pm 0.03$  mol/l =  $0.2364 \pm 0.0005$  g/cc or  $V_c = 72.05 \pm 0.08$  cc/mol. It is also shown in Fig. 4.

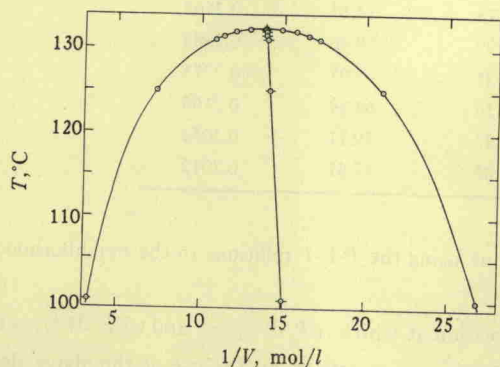


Fig. 4 Law of rectilinear diameters for ammonia

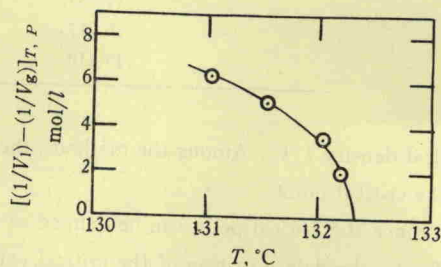


Fig. 5  $[(1/V_l) - (1/V_g)]_{T,P}$  vs. temperature curve

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

Temp. $t$ ( $^{\circ}\text{C}$ )	Saturated vapor pressure, $P$ (atm)	Saturated vapor density, $1/V_g$ (mol/l)	Saturated liquid density, $1/V_l$ (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<sup>1)</sup>.

\*\* These are the extrapolated values of the experimental densities of gaseous ammonia in previous work<sup>1)</sup> 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.

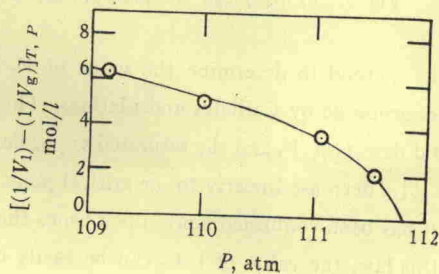


Fig. 6  $[(1/V_l) - (1/V_g)]_{T,P}$  vs. pressure curve