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

The *P-V-T* Relations of Ammonia in the Neighborhood of Critical Point and the Critical Values of Ammonia

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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

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the previous work[1]. Then it is believed that the compressibility factors of ammonia, $Z=Pv/nRT$, 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.

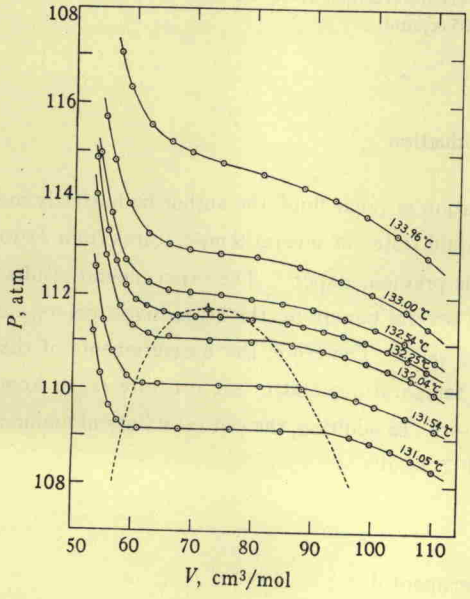

Fig. 1 Isotherms of ammonia in the neighborhood of critical point

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 ⊕ 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