

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

The 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)