Studies on the P-V-T Relations of Fluids at High Pressure I

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Teflon rings containing 30% glass-fiber by weights were used for packing between the piston and the cylinder and they were set so well that the inner volume change of the piezometer by the transformation of the packing would be negligibly small. The moving distance of the piston stroke (200 mm in maximum) was measured within an error of 0.02 mm by the depth gage fixed on the top of the screw rod. The inner volume of the piezometer from 15 to 35 cm³ can be changed by moving the piston up or down to change its position against the cylinder. The relation between the inner volume of the piezometer and the positions of the piston was determined by the calibration described later. The parts of the apparatus for measuring both the pressure and the mass of the sample are the same as those for the gaseous ammonia mentioned in the previous section.

The operations are as follows: After sufficiently evacuating the inside of the piezometer, any desired amount of liquid ammonia sample is introduced into the piezometer by distillation. Then, the valve (V_1) is closed and the valve (V_2) is opened. The temperature of the oil thermostat is raised slowly from room temperature to the desired temperature, while the vapor pressure of the sample and the oil pressure in the tubing of the pressure measurement system are kept to be equal by handling the oil injector (E).

The temperature of the thermostat is kept constant at the desired value, then the piston is pushed very slowly into the cylinder and the sample is compressed. The volumes of the compressed liquid ammonia in any piston-positions can be obtained to read the readings of the depth gage.

The pressures of the sample are measured by the pressure balance (D) through the pressure difference detector at the same time. Finishing the compression process, the volume and the pressure relation in the expansion process is measured in the similar manner mentioned above by pulling the piston out. In these processes, it was assumed that the temperature of the sample reached in equilibrium with the temperature of the thermostat when the pressure of the sample became constant within the change of 0.01 atm.

Both measured values of the pressure at the same volume in the compression and the expansion processes always agreed well within 0.01 atm which was the experimental error in the pressure measurements. Finally, the sample is introduced into the low pressure system of glass and its amount is measured by the same operation as the measurement for gaseous ammonia.

Precision on the measurement: The volumes of the piezometer correlative with the piston stroke were determined at 50 and 100°C using 99.99% pure nitrogen by the same operation as for the constant volume method*.

The inter- and extrapolated values were used for the volumes at other temperatures. It resulted that they could be taken as the linear functions of the piston stroke within the error of 0.1% up to 500 atm. The errors for other measurement variables were the same as for the cases of gaseous ammonia. It is believed that the compressibility factor of liquid ammonia would be obtained experimentally by this apparatus and operation within the error of 0.2% in maximum, calculated from the above errors which were accompanied with the measured pressure, volume and temperature values.

^{*} For the compressibility factor of nitrogen at 50 and 100°C, the values by our previous work⁵) were used for the pressure ranges up to 100 atm and the values by Michels^{6,7}) were used abuve 100 atm, respectively.

K. Date

Purity of ammonia

Commercial ammonia was purified by repeated distillation and dehydrated by metallic sodium. It was used for the sample ammonia in this study. The amount of the innert gases in it was determined to be less than 0.04% by gas adsorbing analysis. It is believed that the sample is sufficiently more than 99.9% in purity.

Results and Discussions

Gaseous ammonia

The *P-V-T* relations of gaseous ammonia were measured at 25, 50, 75, 100 and 125°C up to the neighborhood of each saturated vapor pressure. The smoothed values of the compressibility factor of ammonia were obtained graphically from a lot of the experimental data. They are shown in Tables 1 and 2, vs. pressure and density respectively. All of the deviations between the experimental and smoothed values are less than 0.1%.

There are not so many experimental works for the P-V-T relations of gaseous ammonia reported by other workers. The data given by Meyers and Jessup⁸) (-35 to 300°C, 85.5 to 1300 cc/g, 0.865 to 28.378 atm) and by Beattie and Laurence⁹) (50 to 325°C, 20 to 95 cc/g, 14.37 to 130.40 atm) can be taken for the comparison with these results in the ranges of these experimental pressure and temperature conditions. And, also, the compressibility factor of gaseous ammonia had been measured preparatively in this laboratory in the ranges of 25 to 125°C and up to 45 atm by the variable volume method using the glass-piezometer and mercury-piston⁵). The data of this work were compared with the above three previous data.

They are shown in Table 3 in terms of the compressibility factor and the deviations from those of this work at each pressure and temperature. It is shown that the data given by Meyers and Beattie agree with those of this work with the deviations of about 0.2% through their almost whole ranges of the experimental conditions excepting with the deviations of 0.4 to 0.5% in the neighborhood of the saturated vapor pressures at 25 and 75°C, and that the data of our previous work are in fair agreement with those of this work at each pressure and temperature except in the neighborhood of the saturated vapor pressures at 50 and 75°C. The facts that the data of our previous work had considerablly smaller values than of this work and of Beattie and Laurence in the neighborhoods of the saturated vapor pressures at 50 and 75°C, can be understood as follows: the previous measurements were made by the method which was to measure optically or electrically the volume of sample ammonia compressed by mercury piston into the glass-piezometer. Approaching near to the saturated vapor pressures, it was afraid that the sample ammonia might be caught partly into the mercury becoming fine mists. Therefore, it is considered that the previous values were measured too small in these pressure ranges at 50 and 75°C.

⁸⁾ C. H. Meyers and R. S. Jessup, Refrig. Eng., 11, 345 (1925)

⁹⁾ J. A. Beattie and C. K. Laurence, J. Am. Chem. Soc., 52, 6 (1930)