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

5

follows. The high pressure gas, of which the compressibility factor is accurately known, is introduced into the pipet. Then, its *P-V-T* relations are measured in the same operation on the measurement of the compressibility factor for ammonia gas. Thus the volume v_1 can be calculated using these data. In this work, it was determined at temperatures 50 and 100°C and pressures up to 100 atm using 99.99% pure nitrogen*. It resulted that Δv_2 , the change in volume of the pipet with the pressure change from 1 atm, was negligibly small up to 100 atm. The values of Δv_1 (the change in volume of the pipet with the temperature change from 50°C) at 25, 75 and 125°C were determined to inter- and extrapolate the experimental values of Δv_1 at 50 and 100°C in regard to temperature.

The volume V_2 can be calibrated seperately to divide into three parts, namely, the volumes of glass cylinders, the volume of gas phase in the left leg of mercury manometer (H) and the volume of the connecting capillary. First, the volume of each glass cylinder was calibrated to measure the weight of the water which was filled in the cylinder at a constant temperature. They were determined for 300 ± 0.02 to $1,000\pm0.08$ cm³ respectively, that is, within an error of 0.01%. Second, the volume of gas phase in the left leg of the manometer (0 to 60 cm^3) was calibrated in an error of $\pm 0.01 \text{ cm}^3$ to measure the weights of mercury filled in the leg on which the scale was marked. Last, some amount of nitrogen filled in any glass cylinder at known pressure and temperature was expanded into the connecting capillary which was evacuated previously, and its pressure change was measured. Then, the volume of the connecting capillary was determined for $14.50\pm0.2 \text{ cm}^3$ by the calculation to make use of their values of the pressure change, the temperature and the volume of the glass cylinder.

The temperatures of each thermostat and the connecting capillary, T_1 , T_2 and T_3 , respectively, were measured to 0.01°C by the mercury thermometers which were calibrated within the errors of 0.03°C in 0 to 50°C range, 0.04°C in 50 to 100°C range and 0.05°C in 100 to 150°C range at the National Research Laboratory of Metrology. Measuring the temperatures at several positions in both thermostats by the high sensitive thermistors, it was assured that their temperatures were constant and uniform within 0.01°C throughout this experimental work.

In the facts mentioned above, it is believed that the compressibility factors for gaseous ammonia would be obtained experimentally by this apparatus and operation within an error of 0.2% in maximum, calculating from the above errors which were accompanied with the experimental pressure, volume and temperature values.

Method for liquid ammonia

In the case of the measurement of the compressibility factor or the specific volume for liquid ammonia, the apparatus and method of the variable volume type are more suitable than the constant volume type. In this method, the compressibility factor or the specific volume for any liquid sample is determined to measure the pressure-volume relations for any known amount of the sampe at the

^{*} In our previous work⁵⁾, the comressibility factors of nitrogen were measured at 50 and 100°C and up to 100 atm by the variable volume method. It was shown that these values also agreed well with the values given by Michels^{6,7)}. They were then used for the calibration of the pipet volume in this work.

⁶⁾ A. Michels, H. Wuoters and J. DeBoer, Physica, 1, 587 (1934)

⁷⁾ J. Otto, A. Michels and H. Wouters, Phys. Z., 35, 97 (1934)

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known constant temperature in principle. In this study, this method was then adopted and the piezometer shown in Fig. 3 was made for the measurement of P-V-T relations for liquid ammonia. As shown in Fig. 4, the whole apparatus is composed of the piezometer in the oil thermostat connected with the part for measuring the pressure of the sample (shown as steel-tubing side) and with that for measuring the amount of the ammonia sample (shown as glass-tubing side).



The piezometer consists of the 18-8 stainless steel cylinder (B), the well polished and hardened tool steel piston (A) having the screw rod and handle movable by hand, the same pressure difference detector as that in the measurement for gaseous ammonia and some valves.

6