

the desired conditions. Another is the low pressure system (glass-tubing side in Fig. 1) in which the molar quantities of ammonia employed above are determined from the measured values of P , V and T in the expanded state near to 1 atm.

The operations are as follows: After evacuating sufficiently the high pressure gas pipet (A), which has the known volume v , through the valve (V_2), (V_2) is closed and then the sample ammonia is introduced slowly from the sample cylinder (B) into the pipet up to some desired pressures. Simultaneously, the oil pressure in the steel-tubing is raised by handling the oil injector (E) and it is balanced with the pressure of ammonia in the pipet.

As shown in Fig. 2, the pipet has the stainless-steel bellows (C) filled with mercury (B), the capillary and the insulated electrode (A). The sample gas is separated from the pressure-transmitting oil by the bellows and mercury. If the pressure of the sample gas in the pipet is slightly higher than the oil pressure in the capillary, then the bellows is contracted with high sensitivity and the mercury is pushed up in the capillary to touch the lower end of the electrode. If the pressure of the sample gas is slightly lower than the oil pressure, the contact between the mercury and the electrode breaks off. This make-break of the contact takes place with very small pressure difference between both sides of the bellows. So the pressure balancing state can be detected very sharply by the use of the electronic circuit which was reported previously in detail⁴).

When the pressure change of the sample gas in the pipet becomes too small to be detected, it is admitted that the temperature of the sample gas comes to equilibrium with the temperature of the oil thermostat (C). Then the pressure of the sample is measured by the use of the pressure balance (D) and the temperature of the sample is determined to be equal to the temperature of the thermostat which is measured by the mercury thermometer. After that, opening the valve (V_2) very slowly, the sample gas in the pipet is expanded into the low pressure system which was evacuated previously to one hundredth millimeter of mercury.

The low pressure system is composed of seven glass cylinders (G) having the known volume of about 300, 500 or 1,000 cm³ (total volume is about 7,000 cm³), the mercury manometer (H) and the connecting capillary having the inner diameter of 2 millimeters. It is set up in the water thermostat (K) kept constant at 25°C. The pressure of the expanded sample gas in the low pressure system is determined by the use of the cathetometer by measuring the height of mercury in the manometer (H).

By the operations mentioned above, the compressibility factor Z may be obtained as follows:

$$Z = \frac{Pv}{nRT_1},$$

$$\text{with } P = P_1 + P_2 + \Delta P,$$

$$v = v_1 + \Delta v_1 + \Delta v_2,$$

$$n = \left(\frac{P_3}{R} \right) \left(\frac{v_1 + \Delta v_1}{Z_1 T_1} + \frac{Z_2 T_2}{v_2} + \frac{v_3}{Z_3 T_3} \right),$$

4) T. Toriumi, K. Date and H. Iwasaki, *Bull. Chem. Research Institute of Non-Aqueous Solutions, Tohoku Univ.*, **10**, 263 (1961)

- where P : the absolute pressure of the sample [atm],
 P_1 : the pressure reading of the pressure balance [atm],
 P_2 : the atmospheric pressure [atm],
 P_3 : the expanded sample gas pressure [atm],
 ΔP : the pressure difference between in- and out-side of the bellows [atm],
 T_1, T_2, T_3 : the temperatures of the sample in the pipet, the glass cylinders and the connecting capillary, respectively [K],
 Z_1, Z_2, Z_3 : the compressibility factors of the sample at pressure P_3 and at temperatures T_1, T_2 and T_3 , respectively*,
 v_1 : the inner volume of the pipet at 50°C and 1 atm [cm³],
 v_2 : the volume of the glass cylinders and the gas phase in the left tube of the mercury manometer (H) [cm³],
 v_3 : the volume of the connecting capillary [cm³],
 Δv_1 : the change in volume of the pipet due to temperature change from 50°C to T_1 [cm³],
 Δv_2 : the change in volume of the pipet due to pressure change from 1 atm to P [atm],
 n : moles of the sample gas,
 R : gas constant, 82.0567 ± 0.0034 [cm³·atm/mol·deg].

Precision on the measurement: The pressure P_1 was obtained by the measurement with the free-piston type pressure balance which was previously reported in detail⁴.

The pressure balance was calibrated within the error of 0.02% by the use of the standard mercury manometer. The atmospheric pressure P_2 was obtained by the measurement with the Fortin type barometer to the accuracy of 0.1 mmHg.

The expanded gas pressure P_3 was obtained to measure the height of the mercury manometer (H) within the error of 0.05 mmHg by the use of the cathetometer of 1 meter long. The pressure-difference detector composed of mercury, bellows and electrode was found to be sensitive within a pressure-difference of 0.001 atm and to be reproducible within a pressure-difference of 0.01 atm by the test connecting two mercury manometers to the tubings both inside and outside of the bellows.

As shown in Fig. 2, the high pressure gas pipet is composed of 18-8 stainless-steel cylinder which has 40 cm³ of inner volume, two valves for in- and outlet of the sample and the pressure difference detector. The tips and the seats of the spindles of the valves were made of hardened tool steel, so that the volume change of the pipet would be negligibly small in the transformations of these parts.

The inner volume of the pipet v_1 was determined within an error of 0.10% by the operation as

* These values around 1 atm were estimated by the use of the experimental equations given in the previous paper⁵ and used in this work.

5) K. Date and H. Iwasaki, *Annual Report of the Asahi Glass Foundation for the Contribution to Industrial Technology*, **11**, 65 (1965)