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The Sublimation Pressure of Tetrasulfur Tetranitride

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Tetrasulfur tetranitride, S_4N_4, is stable contrary to expectation in air at room temperatures, but it decomposes explosively when struck or when heated above its melting point. Goehring and Voigt[1] pointed out that tetrasulfur tetranitride decomposes into its elements at approximately 130 °C. The concrete values of the sublimation pressure of tetrasulfur tetranitride have not been reported because of its instability, although Meuwsen[2] stated that the compound can be sublimed below 130 °C at 0.1 mmHg.

In this work, the sublimation pressure of tetrasulfur tetranitride was studied at temperatures below 90 °C by means of the method of transpiration.

Experimental

Materials. The tetrasulfur tetranitride was prepared by the method described by Villena-Blanco and Jolly[3] without further purification.

Argon was obtained from the Nippon Sanso Company, which guaranteed a purity better than 99.994%, as a carrier gas. The carrier gas was passed through a cylinder containing silica gel before it was admitted into the reaction vessel.

Procedure. A flow diagram of the apparatus is shown in Fig. 1. The reaction vessel was heated at temperatures from 70 to 90 °C with a precision of ±0.3 °C by mounting it in a thermostated aluminum block. The preheated carrier gas was made to flow, at specified flow rates, through about 3 g of the tetrasulfur tetranitride put on a glass filter in the reaction vessel. The accuracy of the specified flow rates, obtained by using an automatic control valve model BM-N, the Nisshin Kagaku Company, and an argon bomb with a regulator, was of the order of 0.5%. The excessive pressure in the reaction vessel against the atmospheric pressure was measured with a manometer containing a Silicone oil with a low vapor pressure. The pressure control of the carrier gas was not carried out, because the maximum variation in the atmospheric pressure during the runs was 2.5 mmHg (corresponding to about 0.3%). The temperature of the flow gas in the reaction vessel was measured with a thermometer and was maintained within ±0.3 °C. The carrier gas containing the tetrasulfur tetranitride vapor was discharged through a capillary (2 cm in length and 0.1 cm in diameter) into a water-cooled trap. The capillary was heated at slightly higher temperatures than that of the reaction vessel to prevent a deposition of the tetrasulfur tetranitride on it. The total volume of the carrier gas was measured with an accuracy of ±0.4% by using a wet-type gas flowmeter, model WK-0.5, which can be read to an order of 1 ml (Shinagawa Seisakusho).

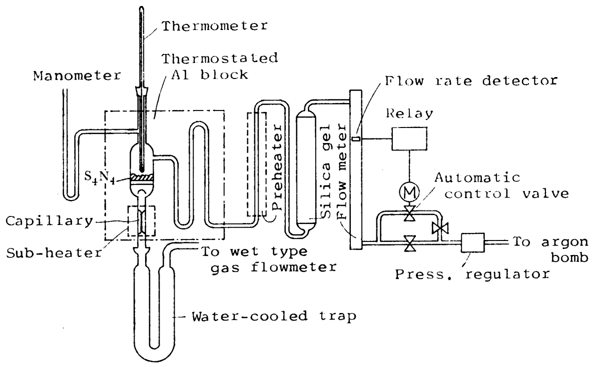

Fig. 1. Schematic diagram of apparatus.

The small amount of the trapped tetrasulfur tetranitride was estimated from the optical absorbance of its benzene solution at 350 mμ by using a working curve previously

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[1] M. Goehring and D. Voigt, *Z. Anorg. Allgem. Chem.*, **285**, 181 (1956).

[2] A. Meuwsen, *Ber.*, **65**, 1724 (1932).

[3] M. Villena-Blanco and W. L. Jolly, "Inorganic Synthesis," Vol. IX, ed. by S. Y. Tyree, Jr., *et al.*, McGraw-Hill, New York (1967), p. 98.

determined (the molar extinction coefficient at 350 mμ was 1057).

Results and Discussion

The melting point of the sample was determined microscopically to be 179 °C by using materials of known melting points as references. The value of the melting point for the tetrasulfur tetranitride which was prepared by the Jolly method was found to be 178—179 °C.[4] The IR spectrum[5] and the X-ray powder diffractogram[6] of the sample showed patterns attributable to tetrasulfur tetranitride only. Therefore, the sample obtained in this work was considered to be pure enough to measure the sublimation pressure of tetrasulfur tetranitride.

An abrupt weight loss and an exothermic change in the thermal gravimetric analysis and the differential thermal analysis on tetrasulfur tetranitride[6] occurred at temperatures above approximately 125 °C. These results were not affected by the presence of air. It is, then, considered that tetrasulfur tetranitride decomposes at temperatures higher than 125 °C. Therefore, the partial pressures of the sample were estimated in the temperature range from 70 to 90 °C.

Quantities of the argon sufficient to trap about 1 mg of the tetrasulfur tetranitride were used in all the runs; *i.e.*, they were in the ranges from 15.30 to 17.03 l (the passing times were from 160.0 to 600.0 min), from 9.274 to 10.99 l (from 105.0 to 510.0 min), from 5.712 to 7.632 l (from 70.0 to 420.0 min), from 3.442 to 5.151 l (from 45.0 to 180.0 min), and from 2.877 to 3.117 l (from 30.0 to 110.0 min) as the standard state at 70, 75, 80, 85, and 90 °C respectively, while the amounts of the trapped tetrasulfur tetranitride were estimated to be in the range from 0.899 to 1.30 mg. The tetrasulfur tetranitride deposited immediately on the neck of the trap as a fine powder after its vapor had passed through the thermostated aluminum block.

The partial pressure, p, of the tetrasulfur tetranitride at the specified temperature and flow rate was calculated by means of the following equation, being assumed to obey the law of partial pressures:

$$p = (P+p')/[1+(184.3/w)(P+p''-p_w)V/RT]$$

where P is the atmospheric pressure; p', the excessive pressure in the reaction vessel; p'', the excessive pressure in the gas flowmeter; p_w, the vapor pressure of water in the gas flowmeter; w, the weight of the trapped tetrasulfur tetranitride; V, the observed total volume of the carrier gas; T, the temperature of the carrier gas in the gas flowmeter, and R, the gas constant.

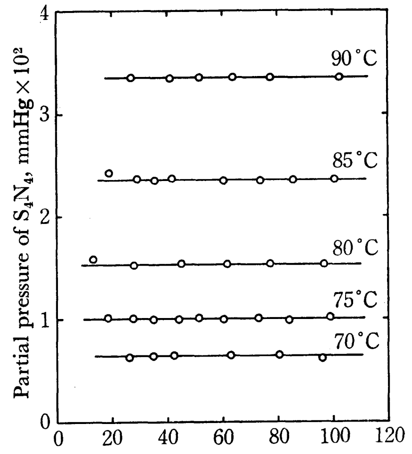

Fig. 2. Dependence of partial pressure of S_4N_4 on flow rate.

The relationship between the partial pressures and the flow rates, which were expressed as the standard states, is shown in Fig. 2. The values of the partial pressure were almost equal to each other at all the temperatures under those conditions except for those at the flow rates of 13.60 ml/min (80 °C) and 19.12 ml/min (85 °C), which were considered to arise from a diffusion[7] of the tetrasulfur tetranitride vapor. Therefore, the average values of the partial pressure can be accepted as those of the sublimation pressure of tetrasulfur tetranitride; they are shown in Table 1. No changes in the structure or chemical components of the sample remaining in the reaction vessel were found by X-ray powder diffraction analysis after the measurements.

TABLE 1. SUBLIMATION PRESSURES OF TETRASULFUR TETRANITRIDE

Temp., °C	Sublimation Press., mmHg
70	6.42×10^{-3}
75	1.00×10^{-2}
80	1.53×10^{-2}
85	2.35×10^{-2}
90	3.51×10^{-2}

The heat of the sublimation, ΔH^s, of tetrasulfur tetranitride in the temperature range from 70 to 90 °C was estimated to be 21.2 kcal/mol from the excellent linear relationship of the Clausius-Clapeyron plot. Although Barker *et al.*[8] deduced the heat of the sublimation of tetrasulfur tetranitride to be 15±5 kcal/mol from the results obtained by using a bomb calorimeter, the value estimated in this work is slightly larger than that obtained by Barker.

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[4] W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J. (1970), p. 502.

[5] H. G. Heal, "Inorganic Sulfur Chemistry," ed. by G. Nickless, Elsevier, Amsterdam (1968), p. 464.

[6] S. Hamada, A. Takanashi, and T. Shirai, This Bulletin, **44**, 1433 (1971).

[7] U. Merten, *J. Phys. Chem.*, **63**, 443 (1959).

[8] C. K. Barker, A. W. Cordes, and J. L. Margrave, *ibid.*, **69**, 334 (1965).