THE VISCOSITY AND THERMAL STABILITY
OF VAPOR OF TRIMETHYL BORATE

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To concentrate boron isotope of mass 10, trimethyl borate vapor was proposed as suitable for the separation by thermal diffusion. The viscosity was measured after Melaven and Mack for 50–400°, and is expressed in the empirical formula $\eta = 0.789 \times 10^{-4}(T/273.14)^{0.96 \pm 0.04}$ (poise). The thermal diffusion coefficient α calculated from $n = 0.96$ after Furry and Jones, is 2.80×10^{-4}, which suggests that this vapor is not suitable, in this point of view, for thermal diffusion separation. Trimethyl borate vapor was found to be stable up to 470° even in contact with platinum wire.

Because of its large cross-section for the ^{10}B-$(n,\alpha)^7$Li reaction, boron of mass 10 has a considerable importance in measuring slow neutrons in nuclear research or industry. Though several methods have been proposed to concentrate this isotope of boron, such as distillation of boron trichloride,[1] thermal diffusion of boron trifluoride[2] and others, their separation factors are very poor, unfortunately. The thermal diffusion of a suitable gaseous compound is one of the universal methods for separating isotopes, and some available gaseous compounds are to be sought, which are stable over a sufficiently large temperature range, and the coefficient of viscosity of which is not near to unity.[3] Moreover, easiness for handling and low molecular weight are desired, too.

Because of its rather lower molecular weight and small hygroscopicity, trimethyl borate was proposed by the present authors and in this paper we report measurements on the viscosity and thermal stability of trimethyl borate, which were as yet unknown. The suitability for thermal diffusion is also discussed.

Experimental

The viscosity of trimethyl borate vapor was measured after Rankine[4] and Melaven and Mack[5] for 50–400°. Its thermal stability was also observed in the presence of platinum wire up to 470°.

Material Used.—Trimethyl borate was prepared from boric acid anhydride and methanol after the method of Schlesinger, *et al.*[6] The azeotropic mixture of borate and methanol was split into two liquid layers by adding calcium chloride or lithium chloride, and the upper layer was redistilled. This purification was repeated several times. The distillate contained a trace of methanol, and its vapor pressure was found slightly higher than that measured by Webster[7] and Wiberg.[8] So, adding metallic sodium to it and fixing methanol as sodium methylate, distillation was repeated in a vacuum train until the vapor pressure became constant and agreed well with that of the above-mentioned authors. Its final value fell just between those observed values.

Total boron was analyzed by usual acidimetry with the addition of glycerol after hydrolysis with water. The purity of this product was found to be 100% within the experimental error.

Apparatus and Measurement

Viscosity.—The apparatus for measuring the viscosity was nearly the same as that of Melaven and Mack,[5] and was made all of borosilicate glass. No greased tap was used. Of course, the sample was introduced under vacuum to eliminate moisture, and the inlet tube was sealed off after introduction. The radius and the length of the capillary through which the vapor flowed were 0.1615 ± 0.0015 mm. and 200.4 mm., respectively. The capillary was heated by an electric furnace, specially designed so as to have uniform temperature distribution along the tube. Furthermore, the whole was kept in an air thermostat, operated by a well stabilized power supply. Temperature was measured with calibrated thermometer or thermocouple. Its accuracy was within ±0.5°, which was sufficient for the present purpose.

The evaporating tube and the condensing tube were submerged in a water thermostat and in a freezing mixture in Dewar vessel, respectively, and the vapor pressure in these tubes was measured with the usual mercury manometers and a cathetometer. The quantity of gas which flowed through the capillary was determined by measuring the volume decrease of liquid in the evaporation tube with a cathetometer. The pressure drop along the capillary, and the quantity of gas which flowed through it was ordinarily 20–50 mm. and 3–7 mg./min., respectively. Benzene was adopted as standard for calibrating the capillary, as its viscosity up to 250° was well known.[9] The coincidence between our observed value and that of Nasini was fairly good.

Measurement of Thermal Stability.—The apparatus as in Fig. 1 was constructed. Sample was sealed in this all-glass vessel and condensed in B. Then, B being heated and A being cooled, the sample was transferred from B to A through heated tube in electric furnace, in which a platinum wire was inserted as shown in Fig. 1. After each transfer operation from B to A, or reversely, from A to B, which required about half an hour, the vapor pressure was measured by the mercury manometer D, to ascertain whether there occurred any decomposition or not.

Results and Discussions

Observed values were calculated with the usual formula,[5] in which the correction for slippage was considered. Viscosity of trimethyl borate for 50–400° was plotted as in Fig. 2. When the correlation between η and T is expressed as following the empirical formula

$$\eta = \eta_0 \left(\frac{T}{T_0}\right)^n \qquad (1)$$

where η is viscosity in poise, T is temperature in Kelvin and $T_0 = 273.14°$ K., we obtain for 50–400°, with the aid of the method of least squares

$$\left. \begin{array}{l} n = 0.96 \pm 0.04 \text{ (mean standard deviation)} \\ \eta_0 = 0.789 \times 10^{-4} \text{ poise} \end{array} \right\} \quad (2)$$

When this result is expressed in Sutherland's formula as

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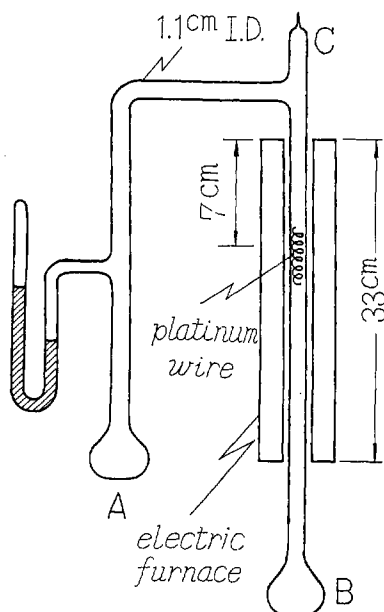(9) A. G. Nasini, *Proc. Roy. Soc. (London)*, **A123**, 692 (1929).

Fig. 1.—Apparatus for the measurement of thermal stability.

$$\eta = \eta_0' \sqrt{\frac{T}{T_0}} \frac{1 + \dfrac{C}{T_0}}{1 + \dfrac{C}{T}} \qquad (3)$$

We obtain

$$C = 398^\circ \text{ K.} \qquad (4)$$

Following Furry and Jones' calculation,[3] the thermal diffusion constant α is expressed as

$$\alpha = \frac{105}{118} \frac{m_2 - m_1}{m_2 + m_1} R_T \qquad (5)$$

where m_1, m_2 are molecular weights of two isotopic gaseous compounds, and R_T is expressed in an approximate equation
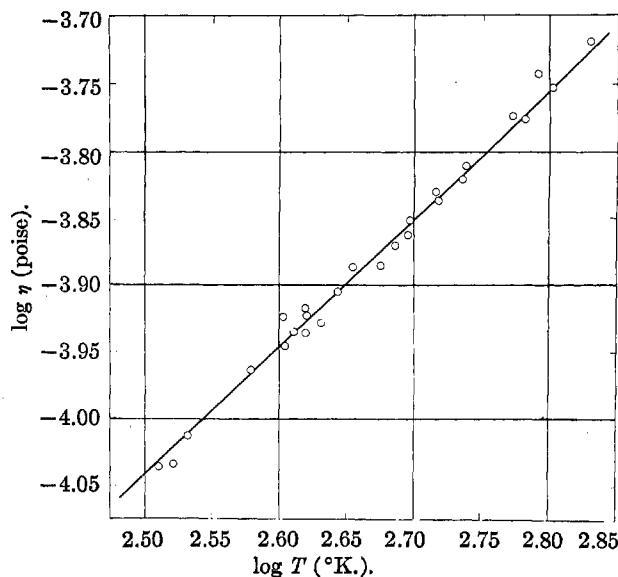
$$R_T \approx 1.7(1 - n) \qquad (6)$$

Fig. 2.—Viscosity of trimethyl borate vapor for 50–400°.

Introducing $n = 0.96$, $m_1 = 103$ and $m_2 = 104$ in eq. 5 and 6, we obtain $R_T \approx 0.06_5$ and $\alpha \approx 2.80 \times 10^{-4}$. These values suggest that trimethyl borate is unsuitable for thermal diffusion, just as is boron trifluoride which was estimated by Watson, et al.[2a]

Thermal Stability.—No change of vapor pressure was observed up to 470° in the presence of platinum wire. The thermal stability of *pure* trimethyl borate is good, but, if a trace of methanol was present, a small quantity of carbonaceous matter was observed on the wall of the glass tube at 300°.

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INTERACTING FLOWS IN DIFFUSION OF
THE SYSTEM RAFFINOSE–UREA–WATER

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Diffusion experiments are reported which establish that the phenomenon of interacting flows exists in the system raffinose–urea–H_2O. The results are interpreted by means of generalized flow equations and the four diffusion coefficients are given for one composition of the system. When studying diffusion of systems of three or more components it is suggested that some method be used to test for the presence of interacting flows.

Diffusion data already have been reported[1-3] to establish the phenomenon of *interacting flows* in the diffusion of certain three-component liquid

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systems. In general such systems may consist of two strong electrolytes in a solvent, a strong electrolyte and a non-electrolyte in a solvent or two non-electrolytes in a solvent. Although the previous data illustrate that measurable interaction of flows may occur in the first two cases, this paper reports data which indicate that, for a system of two non-electrolytes in water, measurable interaction of flows may also exist.