Isotope Effect of Boron in the Thermal Decomposition of the Boron Trifluoride-Calcium Fluoride Compound[*]

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One of the purification methods of boron trifluoride gas for neutron counters involves the thermal decomposition of boron trifluoride-calcium fluoride addition compound[1,2]. In one of the papers describing

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[*] Partly read at the 2nd Symposium of Atomic Energy in Japan, Feb. 1958.

1) A. C. Graves and D. K. Froman, "Miscellaneous Physical and Chemical Techniques of the Los Alamos Project", McGraw-Hill, New York (1952), p. 153.

2) F. Hudswell, J. S. Nairn and K. L. Wilkinson, AERE, C/R 651 (1951).

this process, Hudswell et al.2) reported the unconfirmed, but apparently not erroneous result that at the earliest stage of the thermal decomposition of the boron trifluoride-calcium fluoride compound the fraction of the boron fluoride gas evolved might be enriched in ^{11}B. The present authors attempted to make sure of this fact and found that there is a considerable isotopic fractionation effect in this reaction, to such an extent that this phenomenon might be of use for the isotope separation of boron-10.

The results obtained are shown in Figs. 1 and 2, in which the percentages of boron trifluoride gas evolved are taken at the abscissa in sequence as the gas was evolved, and the isotopic abundance ratios of boron in each fraction in terms of the ratio ^{11}B/^{10}B are taken at the ordinate. The latter was read directly from the height of the peaks of m/e 49 and 48 (due to $^{11}BF_2^+$ and $^{10}BF_2^+$, respectively) in the mass spectrogram.**,*** These ratios can also be estimated by the peaks of m/e 11 and 10, but these peaks are less sensitive than those of 48 and 49, and, as is shown in Fig. 2, the ^{11}B/^{10}B values from these lower m/e regions were smaller than those from the higher regions3).

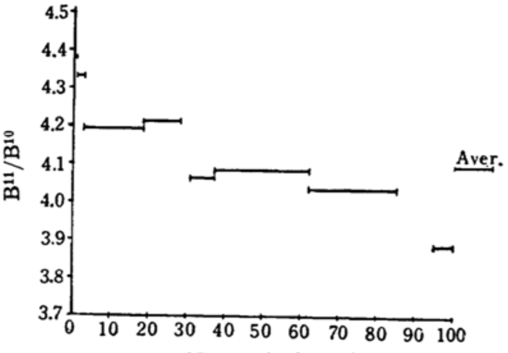

Fig. 1. Isotopic fractionation data for Batch A.†

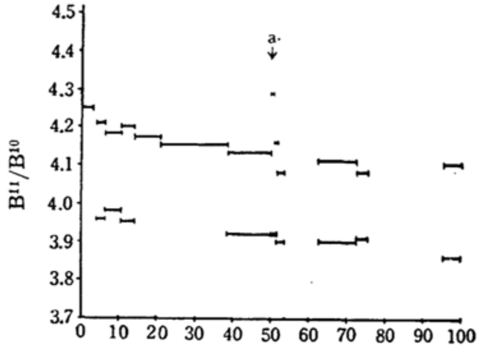

Fig. 2. Isotopic fractionation data for Batch B.†
(The lower group of the plots indicates the values from the peaks of m/e 11 and 10. The point a indicates the interruption of the gas evolution for several days.)

It is no doubt that a significant isotopic effect occurred in this reaction, and the separation factors calculated schematically reach 1.035 in Batch A and ca. 1.015 in Batch B. As this factor is considered to depend on the speed of evolution of the gas, it was kept as low as possible, i.e., in the case of Batch A, it was ca. (2 l.)STP/hr, the total gas content in the batch being 0.8 mol. Also, the boron trifluoride is so strongly adsorbed (chemisorbed) on calcium fluoride, that the sampling of the last fraction of the gas, which probably contains ^{10}B most enriched, was sometimes incomplete on account of cracking in the glass vessel by strong heating. Had these difficulties been avoided, the separation factor might have reached a greater value than this. Nevertheless, this observed separation factor in Batch A ($\alpha=1.035$) shows the largest value hitherto reported on the isotopic separation of ^{10}B using chemical exchange reactions5).

The boron trifluoride-calcium fluoride compound was prepared by the method of Graves et al.1) and the original boron trifluoride gas was prepared by Booth's method6). The thermal decomposition of

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** The mass-spectroscopic measurements were done with a 21-103A Type Mass Spectrometer (Consolidated Electrodynamic Corp.) at the University of Tokyo or with a 103 Type Mass Spectrometer (Scientific Research Institute) at Nagoya University.

*** When the peak of m/e 47 was considerably large, correction was made on the observed values of peaks 48 and 49, on the basis that the whole peak of 47 is due to $^{28}SiF^+$, and that $^{29}SiF^+$ and $^{30}SiF^+$ did contribute to the peaks of 48 and 49 respectively, depending on the natural abundance ratio of ^{28}Si, ^{29}Si, and ^{30}Si8). Lately, however, M. Yamane of Hitachi Co., in a personal communication, suggested that the peaks of 46 and 47 are due to $^{10}BF(OH)^+$ and $^{11}BF(OH)^+$. Although this is perhaps true, the tendency of the isotopic fractionation by this process and thus the separation factor do not deviate seriously from the data reported in this paper.

3) W. W. Watson, J. C. Buchanan and F. K. Elder, *Phys. Rev.*, **71**, 887 (1947).

† Batch A was prepared from purified (distilled) boron trifluoride etherate, $BF_3\cdot(C_2H_5)_2O$, and Batch B was from the residue of this etherate distillation. The fact that there is a difference between the average ^{11}B/^{10}B ratios of the two batches (Figs. 1 and 2 (upper group)) indicates that the isotopic fractionation effect occurred at the boron trifluoride etherate distillation4,5).

4) R. Nakane, T. Watanabe and S. Isomura, ***Report of Scientific Research Institute***, **33**, 330 (1957).

5) International Symposium on Isotope Separation, Amsterdam, 1957.

6) H. S. Booth and K. S. Willson, *J. Am. Chem. Soc.*, **57**, 2273 (1935).

the compound and the sampling of the gas were done in a closed, evacuated apparatus, in which the gas began to be evolved at about 200°C, and evolution did not completely cease even at about 350°C.

The authors believe that this effect is applicable to the practical separation of boron 10, the scheme of which and some fundamental data for which will be reported later.

In this connection, the authors wish to call attention to the expectation that, in regard to substances which contain the comparatively lighter atomic weight elements such as lithium[7] and boron, their isotopic abundance ratio may possibly change appreciably by a simple procedure, such as vaporization, recrystallization or adsorption. As for boron, its well known indefinite atomic weight due to various geological origins[8] has, without doubt, much connection with this inference.

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[7] A. E. Cameron, *J. Am. Chem. Soc.*, **77**, 2731 (1955); G. Wagner and A. Pelz, *Monatsh*, **86**, 414 (1955) [*Chem., Abstr.* **50**, 692h (1956))], etc.

[8] H. G. Thode, J. Macnamara, F. P. Lossing and C. B. Collins, *J. Am. Chem. Soc.*, **70**, 3008 (1948); H. V. A. Briscoe, P. L. Robinson and H. C. Smith, *J. Chem. Soc.*, **1927**, 282, etc.