

## An Investigation of the Isotopic Constitution of Boron

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When conducting a mass-spectrometer measurement of the isotopic constitution of boron (the compounds of boron were ionized with an electron beam), an effect was observed which depended upon the isotopic distribution. The resulting investigation of this effect showed that during the evaporation of the boron compounds from the platinum oven, vapors of the heavy isotope appeared preferentially, which is an effect opposite to that which should be observed during an ideal evaporation. It was found that in the preparation of gaseous and solid boron compounds a similar separation of the isotopes occurs with the same sign for the separation coefficient. The influence of the indicated distribution effect on the accuracy of the determination of the isotopic constitution of boron was investigated.

IN the work of Inghram<sup>1</sup> on the relative concentrations of the two isotopes of boron with masses 10 and 11, the value  $^{11}\text{B}/^{10}\text{B} = 4.31_1 \pm 0.017$  was quoted. Recently, Osberghaus<sup>2</sup> has repeated the measurement using a commercial product, with six different compounds of boron, and has obtained the value  $^{11}\text{B}/^{10}\text{B} = 4.11 \pm 0.04$ . In reference 3, where compounds different from those employed by Osberghaus were used, the values  $^{11}\text{B}/^{10}\text{B} = 4.269$  to  $4.420$  were obtained. On the basis of these results one can draw the conclusion that the diversity of the experimental data for the ratio  $^{11}\text{B}/^{10}\text{B}$  obtained in the various experiments is due not only to the actual different isotopic constitution of the various samples with different origins, but also to systematic errors. One must assume that the preparation of the compounds resulted in changes in the isotopic constitution of the boron, and that for this reason it is necessary to apply special methods. For the solution of this problem it is necessary to conduct experiments with various compounds of boron. The measurements were taken by the same method with two spectrometers that are described by the author and Ordzhonikidze<sup>4</sup>.

Our measurements utilized a series of boron compounds with different origins: compounds of amorphous boron (Kalbaum), boron hydroxide  $\text{B}(\text{OH})_3$ , boron sesquioxide  $\text{B}_2\text{O}_3$  and potassium-borofluoride  $\text{KBF}_4$  (Glavkhimreaktiv). The  $\text{BCL}_3$  was prepared from amorphous boron by chlorination, and the oxides of boron were taken from a wet stream of oxygen over  $\text{B}(\text{OH})_3$ . The  $\text{Na}_2\text{B}_4\text{O}_7$

TABLE I

Type of Ions	$^{11}\text{B}/^{10}\text{B}$
$\text{B}^+$ . . . . .	$4.103 \pm 0.001$
$\text{BCl}^+$ . . . . .	$4.105 \pm 0.005$
$\text{BCl}_2^+$ . . . . .	$4.106 \pm 0.002$

was also obtained from amorphous boron by fusion with sodium in a stream of oxygen. During the manufacture of these substances special attention was paid to letting the reactions be as close to 100% complete as possible. This was done to minimize the possibility of chemical separation of the isotopes. The  $\text{BF}_3$  was obtained from potassium borofluoride either by heating in vacuo or by reaction with dry sulfuric acid.

The two gaseous compounds were investigated first. Using  $\text{BCl}_3$ , the ratio  $^{11}\text{B}/^{10}\text{B}$  was measured for different ions. The results are shown in Table I. The measurements of the  $^{11}\text{B}/^{10}\text{B}$  ratio for  $\text{BCl}^+$  ions were somewhat less accurate because it was necessary to correct for the presence of  $^{13}\text{C}^{16}\text{O}_2^+$  and  $^{12}\text{C}^{16}\text{O}^{18}\text{O}^+$  lines by measuring the intensity of  $^{12}\text{C}^{16}\text{O}_2^+$ . A small systematic change in the relative amounts of the two isotopes can be attributed to a discrimination between two masses in the ion source with ions of different masses being ejected differently, an effect which decreases with increase in the mass being measured. In our measurements such a discrimination could be caused by the magnetic fields of the ion source (for our mass-spectrometer  $H \sim 150$  oersteds, for a constant accelerating potential of  $\sim 2500$  volts). The measured value of the ratio  $^{11}\text{B}/^{10}\text{B}$  using  $\text{B}^+$  and  $\text{BCl}_2^+$  ions does not change when either the electron energy is changed between 30 and 150 ev or the reservoir

<sup>1</sup> M. G. Inghram, Phys. Rev, 70, 119, 653 (1946).

<sup>2</sup> O. Osberghaus, Z. Physik 128, 366 (1950).

<sup>3</sup> H. G. Thode, J. Macnamara, F. P. Lossing and C. B. Callins, J. Amer. Chem. Soc. 70, 3008 (1948).

<sup>4</sup> K. Ordzhonikidze and V. Shiuttse, J. Exper. Theoret. Phys. USSR 29, 479 (1955); Soviet Phys. 2, 392 (1956).

pressure is change by factors of 150-200. This eliminates the possibility that the measured isotope ratio could be affected by the formation of an extraneous ion layer on the line of mass 10. Lines due to the ions  $^{20}\text{Ne}^{++}$  and  $\text{FH}^{++}$  could be superimposed on the boron line of mass 10. However, Ne was absent from the apparatus and the presence of  $\text{FH}^{++}$  was excluded by the use of chlorinated boron compounds.

Due to the possibility of isotope separation in the accelerating region of the ion source, we should choose as the more reliable value of  $^{11}\text{B}/^{10}\text{B}$  the value obtained with the largest mass, i. e. for

$\text{BCl}_2^+$ . Here  $^{11}\text{B}/^{10}\text{B} = 4.106 \pm 0.002$ , which agrees very well with the value given in reference 2.

TABLE II

Type of Ions	$^{11}\text{B}/^{10}\text{B}$
$\text{B}^+$ . . . . .	$4.305 \pm 0.002$
$\text{BF}^+$ . . . . .	$4.306 \pm 0.005$
$\text{BF}_2^+$ . . . . .	$4.302 \pm 0.03$

The results of measurements with  $\text{BF}_3$ , obtained from  $\text{KBF}_4$  (Glavkhinreaktiv), are shown in Table II. Measurements with  $\text{BF}^+$  ions have to be corrected for the  $\text{COH}^+$  line, and hence are less accurate. Ions from  $\text{Si}^+$  to  $\text{SiF}_3^+$  were not observed, since glass was never used in the apparatus. Our measurements are remarkably close to the results in reference 1. Hence, the results shown in Table II coincide exactly with those of (1), while the results of Table I agree equally well with reference 2. The results of Tables I and II differ, however, by an amount almost 34 times as large as the sum of the experimental errors. The superposition of the  $\text{HF}^{++}$  line would have shifted the result in just the opposite direction. The same comment applies to the boron-hydrogen compounds, which, in the  $\text{BCl}_3$  case should, at the same time, have changed the relative amounts of the chlorine isotopes, and which, in the  $\text{BF}_3$  case, should have given a new line. However, this type of interference was not observed. Osberghaus<sup>2</sup> states in his paper that in his measurements with  $\text{BCl}_3$  he often observed large changes in the isotopic constitution (up to 8%) without finding any explanation for this phenomenon. In view of this result, he regards the measurements with  $\text{BF}_3$  as more accurate. However, we did not observe changes in the isotopic abundance of

boron if in the measurements we used  $\text{BCl}_3$  and  $\text{BF}_3$  compounds prepared by methods which give a 100% yield. But if we purposely produced fractionation by thermal dissociation, then we got unexpectedly high values for the isotope ratio, as shown by the following experiment. Into a quartz or nickel tube we put a small amount of  $\text{KBF}_4$  or  $\text{NaBF}_4$ , which gave rise to  $\text{BF}_3$  at a pressure of 1 atmosphere in the system used for storage and preparation of samples for the mass-spectrometer. The  $\text{KBF}_4$  and  $\text{NaBF}_4$  were not entirely dissociated at once, but in steps, giving 10 fractions at about 1 atmosphere each. The isotope ratio was measured in all the 10 fractions. The results are shown in the graph of Fig. 1.

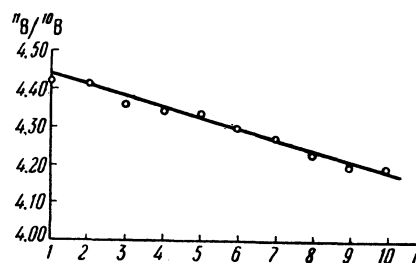


FIG. 1. Dependence of isotopic constitution of B in  $\text{BF}_3$  on the number of the fraction.

As is evident from the figure, there is a significant amount of isotope separation,  $^{11}\text{KBF}_4$  dissociating initially more than  $^{10}\text{KBF}_4$ , in contradiction to what one expects from kinetic considerations. From this it follows that if, when samples are prepared, 100% yield is not guaranteed, (which is difficult to do with boron), then significant, systematic and hard to control errors can creep in. In order to have full confidence in our results, in addition to measurements with gaseous compounds of boron, we also sublimated solid boron compounds in the ion source. The sesquioxide  $\text{B}_2\text{O}_3$  and dry borax  $\text{Na}_2\text{B}_4\text{O}_7$  were placed in a platinum crucible and evaporated. The isotopic constitution of boron was measured using  $\text{B}^+$  ions. The results were corrected, if accuracy so required, for the discrimination effect of about 0.8%. The results of these measurements are shown in Table III. The measurements on  $\text{Na}_2\text{B}_4\text{O}_7$  and especially on  $\text{B}_2\text{O}_3$  are less accurate because we could not keep the ion currents sufficiently constant. Nevertheless, the measurements confirm our previous result and clearly show that the isotopic constitution of both types of boron varies by almost 5%.

TABLE III

Substance	Compound Measured	$^{11}\text{B}/^{10}\text{B}$
a) Boron (Kal'baum)	$\text{BCl}_3$ . . . . .	$4,106 \pm 0,002$
" "	$\text{B}_2\text{O}_3$ . . . . .	$4,11 \pm 0,01$
" "	$\text{Na}_2\text{B}_4\text{O}_7$ . . . . .	$4,108 \pm 0,007$
b) Boron (Glavkhimreaktiv)	$\text{BF}_3$ . . . . .	$4,308 \pm 0,003$
" "	$\text{B}_2\text{O}_3$ . . . . .	$4,30 \pm 0,01$
" "	$\text{Na}_2\text{B}_4\text{O}_7$ . . . . .	$4,305 \pm 0,005$
c) Mixture of 56% a) and 44% b)	$\text{Na}_2\text{B}_4\text{O}_7$ . . . . .	4,183
d) by computation	—	4,189

It should be noted that these results are confirmed by observations on the halides of lithium, described in reference 4, where the same systematic changes in isotopic constitution occur upon evaporation. It is impossible to draw conclusions directly from the measurements, because the boron measurements are much less accurate than the lithium ones. We cannot say here how big the separation coefficient is, but the very fact of separation upon evaporation is shown by the following experiment. In an ideal evaporation the residue should gradually be enriched in the heavy isotope. This process is governed by Raoult's law for ideal distillation, with the condition that the vapors of both isotopes have the same pressure. In the previous work this ideal case was shown to hold for the evaporation of  $\text{Li}^+$  ions from a tungsten surface. When  $\text{LiCl}$  is evaporated the heavy isotope enrichment in the residue becomes observable only when the residue is almost gone, and then the ion currents become unstable, so that it is not possible to make good measurements. In 2 out of 30 experiments

it was possible to get a change in the ratio of  $^{11}\text{B}/^{10}\text{B}$  as the  $\text{B}_2\text{O}_3$  was sublimated. One of these cases is shown in Fig. 2. As before, the curve is opposite to what one would expect theoretically. This means that when  $\text{B}_2\text{O}_3$  (or  $\text{Na}_2\text{B}_4\text{O}_7$ ) is ideally sublimated more molecules with  $^{11}\text{B}$  go into the gaseous phase than molecules

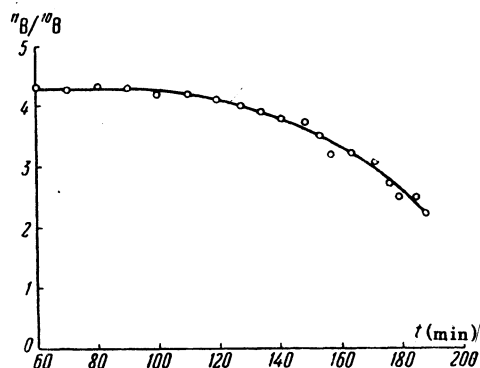


FIG. 2. Dependence on time of the isotopic constitution of B in the evaporation of  $\text{B}_2\text{O}_3$ .

TABLE IV

Substance	Source	$^{11}\text{B}/^{10}\text{B}$
Amorphous boron	Kal'baum . . . . .	4,106
Crystalline boron	Shering-Kal'baum . . . . .	4,100
Boric oxide	" "	4,112
Boron carbide	?	4,238
Borax	Glavkhimreaktiv . . . . .	4,232
Boric oxide	" "	4,240
" "	" "	4,308
" "	" "	4,241
" "	" "	4,461

with  $^{10}\text{B}$ . We should note that when  $\text{BF}_3$  or  $\text{BCl}_3$  were fractionated, the backwards effect was again observed<sup>5</sup>.

The results of measurements on a number of technical compounds of boron which were available to us are shown in Table IV.

From the above it is evident that the agreement between the original measurements of Osberghaus and Inghram was fortuitous. It appears that there are systematic differences in the value of  $^{11}\text{B}/^{10}\text{B}$  between boron samples from Central Asia (Glavkhimreaktiv) and boron samples of presumably Italian origin (Kalbaum). The Italian boron has an isotope ratio of about  $4.10 \pm 0.02$ , while the central Asiatic boron has  $4.25 \pm 0.05$ .

The differences obtained between the various other boron  $\text{KBF}_4$  samples are presumably due to various subsidiary chemical reactions leading to an enrichment of the heavy isotope. Experiments in separating out boron from various minerals, with the purpose of avoiding isotope separation, have so far not been successful. For these reasons we must consider the measurements of Osberghaus as unsatisfactory, while the measurements of Thode and Macnamara are probably high due to various subsidiary separation effects.

A significant part of the measurements described in this paper were made by K. Kupriianov and L. Chernov, to whom the author expresses his gratitude.

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<sup>5</sup> M. Greene and G. R. Martin, *Trans. Farad. Soc.* **48**, 416 (1952).

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