[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

# The Mass Spectrum of Monoisotopic $B_2^{10}H_6$

BY FRANCIS J. NORTON

The dissociation of complex molecules by electron impact presents many features of theoretical and practical interest. This is particularly so in the cases where isotopes occur in the molecular structure. The availability of stable separated isotopes from the Atomic Energy Commission renders possible the construction of molecules with altered isotope ratios. This paper is to report the investigation of one of these, $B_2^{10}H_6$, by the mass spectrometer, and the determination of its molecular fragmentation pattern under electron impact. Normal $B_2H_6$ with its pattern was also studied.

Normal boron consists of two stable isotopes, about 20% $B^{10}$ and 80% $B^{11}$. From the Isotopes Division, U. S. Atomic Energy Commission, was obtained the complex $BF_3 \cdot CaF_2$. In this the boron is 96% of the $B^{10}$ isotope and 4% of $B^{11}$. Through the kindness of Dr. Edith Boldebuck and Dr. J. R. Elliott of our laboratory, $B_2^{10}H_6$ was synthesized from this enriched isotopic material and was used in these experiments.

The mass spectrum of normal polyisotopic diborane has been studied by J. A. Hipple[1] and by Vernon H. Dibeler and Fred L. Mohler.[2] From its mass spectrum they made calculations for the ion distribution of the monoisotopic material. The present work renders possible a comparison between such a calculation and an experimental determination on essentially monoisotopic diborane. Further interest lies in the fact that the mass spectrometers used in references,[1,2] and in the present work were made by three different manufacturers.

## Experimental

(a) The synthesis of $B_2^{10}H_6$ was from the complex $B^{10}F_3 \cdot CaF_2$ (the boron consisting of 96% $B^{10}$). This was heated to 350° in a stream of purified nitrogen. The $B^{10}F_3$ evolved was collected in cooled ether and reacted with lithium hydride. The diborane was separated from the ether and subjected to several low temperature vacuum distillations. It was kept stored at −20°. From mass spectrometer analyses higher boron hydrides and normal $B_2H_6$, if present at all, were under 0.05%. Diethyl ether was under 0.1%, and a small amount, under 0.1%, of $SiH_4$, was also found. Normal $B_2H_6$ was furnished by Dr. L. V. McCarty of our laboratory and was of very high purity.

(b) The mass spectrometer used was the 60° type, single focussing with 6-inch radius of curvature. It is manufactured by the General Electric Company. The accelerating voltage was 2000, ionizing voltage 70. The filament current was 4.5 amperes, total emission current 1.0 ma., trap current (electrons collected at end of ionizing chamber) 0.28 ma. Positive ion currents at the collector were measured by a 954 preamplifier tube in a direct current feedback amplifier circuit. The initial voltage drop to ground was through an IRC resistor of 2 × $10^9$ ohms. The amplifier output was recorded on a General Electric photoelectric recorder with appropriate resistances for selecting sensitivity ranges. The range of masses was covered by sweeping the magnetic field. This could be done either automatically or manually. For precise measurement, the desired peak was selected and held at maximum value on the recorder by manual control. It was focussed to maximum value by manipulating the focussing, drawing out and beam centering voltages.

It should be pointed out that with this type of instrument, to obtain the maximum peak height as is done with these manual measurements reported, refocussing is needed particularly at the lower end of the mass scale, for each mass peak. This means that the scan does not represent the maximum height of peak attainable. The peak heights for a given focus do remain reproducible, and the scans in the lower mass regions especially, should be regarded as recognition patterns. On automatic sweep, changes in focus were made for peaks in the 1, 2, 10–13 and 20–28 mass regions, to give them maximum values possible with fewest focus changes.

The height could be read to ±1% for deflections of the recorder pen from one-half to full scale. For measurements, readings were made in the region of 80 to 100% full scale deflection. This could be chosen by using appropriate, known values of resistance in the measuring circuit.

The gas to be measured was fed into the spectrometer through an orifice type leak. This was so small that 40 mm. gas pressure on the high side gave 2 × $10^{-7}$ mm. on the ion gage at the spectrometer tube outlet. The gas used during analysis was minute in amount. With that leak, the change in pressure in a 1 liter reservoir was under 2% per twenty-four hours.

Measurements were made keeping the $B_2H_6$ on the leak at 25°. I had found in previous work that with very pure, normal diborane handled with good vacuum practice so that the amount of water present is exceedingly small, the following rates of decomposition were observed at an initial pressure of 33 mm. This extrapolated to 25° on a log rate *vs.* $1/T$ plot gives about $10^{-6}$ mm./min., or under 0.005% per twenty-four hours.

| °C. | Rate of pressure increase $dp/dt$ (mm./min.) |
|---|---|
| 120 | 0.045 |
| 110 | .020 |
| 100 | .005 |

Before introduction, the hydride was held in a trap at −190° and any traces of gaseous hydrogen pumped away; it was then taken over to the leak reservoir with the trap at −78°. After the mass spectrum was run, the remaining $B_2H_6$ was taken back into the trap, put at −190° and any hydrogen measured. It was under 0.1%. Hence, it is believed the hydrogen ion peaks found are from $B_2H_6$ dissociation in the mass spectrometer only.

## Results

The isotopic constitution of the gas molecules entering the spectrometer can be calculated very simply from statistical considerations alone. The general expression from simple probability for the abundance distribution of isotopic species of molecules is given by $(a + b)^n(c + d)^m$ where $a$ and $b$ are the relative abundances of the isotopes of one atom, in this case boron isotopes 10 and 11, and $c$ and $d$ are the relative abundances of the stable

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(1) J. A. Hipple, Jr., *Phys. Rev.*, **57**, 350 (1940).

(2) V. H. Dibeler and F. L. Mohler, THIS JOURNAL, **70**, 987 (1948).

TABLE I

ISOTOPIC CONSTITUTION OF THE MOLECULAR GASES USED

| Molecular type | Normal $B_2H_6$ (20% $B^{10}$) (80% $B^{11}$)<br>Proportion calculation | Per cent. | "Monoisotopic" $B_2H_6$ (96% $B^{10}$) (4% $B^{11}$)<br>Proportion calculation | Per cent. |
|---|---|---|---|---|
| $B^{11}B^{11}H_6$ | 0.8 × 0.8 = 0.64 | 64.0 | 0.04 × 0.04 = 0.0016 | 0.16 |
| $B^{11}B^{10}H_6$ | 2(0.2 × 0.8) = 0.32 | 32.0 | 2(0.04 × 0.96) = 0.0768 | 7.68 |
| $B^{10}B^{10}H_6$ | 0.2 × 0.2 = 0.04 | 4.0 | 0.96 × 0.96 = 0.9216 | 92.16 |

hydrogen isotopes 1 and 2. The exponents $n$ and $m$ represent the number of atoms in the molecule. Taking the relative isotopic abundances as: $B^{10} = 0.2$, $B^{11} = 0.8$, $H^1 = 0.998$, $H^2$ (deuterium) $= 0.02$, the expression becomes for $B_2H_6$: $(0.2 + 0.8)^2(0.9998 + 0.02)^6$. For normal deuterium abundances, the second term may be taken as unity. If for the normal $B_2H_6$ a ratio of $B^{11}/B^{10} = 4.0$ is assumed, the following Table I gives the constitution for the two types of $B_2H_6$.

In the mass spectrometer these molecules are broken up by the impact of 70 volt electrons, and form positive ion fragments of various masses. The relative abundance of each of these is given by the positive ion current at each mass. This current is recorded as peak height, and the mass spectrum is a record of the peak heights or abundance plotted against mass. No way is known to calculate the theoretical abundance of the ion fragments from complicated molecules.

Figure 1 gives a record of the spectra of the two kinds of $B_2H_6$ used. Masses are recorded at the bottom, increasing from right to left, and the peak height is the magnitude of the positive ion current.

The measured values of the mass spectra are given in the following Table II. In each case, the dominant peak is taken = 100.

TABLE II

MEASURED MASS SPECTRA OF

| Mass $m/e$ | Monoisotopic $B_2^{10}H_6$<br>Observed in 96% $B^{10}$ material | Monoisotopic $B_2^{10}H_6$<br>Corrected to 100% $B^{10}$ | Normal $B_2H_6$ 20% $B^{10}$ 80% $B^{11}$ average |
|---|---|---|---|
| 28 | ... | ... | (2.4) |
| 27 | 0.5 | (0.1) | 100.0 |
| 26 | 9.4 | 1.5 | 96.2 |
| 25 | 100.0 | 100.0 | 52.5 |
| 24 | 46.9 | 46.5 | 78.7 |
| 23 | 28.6 | 24.5 | 38.3 |
| 22 | 61.0 | 63.0 | 8.5 |
| 21 | 5.1 | 5.1 | 1.3 |
| 20 | 1.9 | 1.9 | 0.1 |
| 14 | ... | ... | 0.5 |
| 13 | 0.9 | 0.5 | 12.6 |
| 12 | 9.7 | 9.9 | 8.0 |
| 11 | 4.6 | 4.7 | 16.0 |
| 10 | 11.5 | 12.0 | 3.65 |
| 2 | 45.7 | 45.7 | 71.6 |
| 1 | 1.6 | 1.6 | 2.4 |

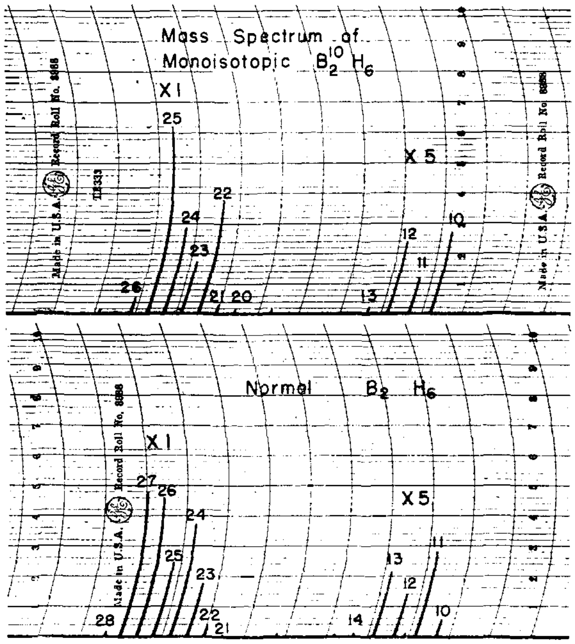

Fig. 1.—The mass spectra of monoisotopic $B_2^{10}H_6$ and of normal $B_2H_6$.

A comparison of reproducibility may be of interest. The following spectra of normal $B_2H_6$ were taken; *a*, *b*, *c* on one day after the gas had run 1, 3 and 5 hours. Spectrum *d* was taken on another day and with another charge of gas.

TABLE III

MEASURED MASS SPECTRA OF NORMAL $B_2H_6$

| Mass | a | b | c | d | Av. |
|---|---|---|---|---|---|
| 28 | 2.0 | 2.0 | 2.0 | 3.7 | (2.4) |
| 27 | 100 | 100 | 100 | 100 | 100 |
| 26 | 95.8 | 96.5 | 96.3 | 96.0 | 96.2 |
| 25 | 52.3 | 52.7 | 53.0 | 51.9 | 52.5 |
| 24 | 78.6 | 79.6 | 79.5 | 77.1 | 78.7 |
| 23 | 37.9 | 38.7 | 38.8 | 37.6 | 38.3 |
| 22 | 8.6 | 8.5 | 8.7 | 8.2 | 8.5 |
| 21 | 1.3 | 1.4 | 1.3 | 1.2 | 1.3 |
| 20 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 14 | ... | ... | ... | 0.5 | 0.5 |
| 13 | 12.5 | 12.9 | 13.5 | 11.6 | 12.6 |
| 12 | 7.9 | 8.1 | 8.4 | 7.6 | 8.0 |
| 11 | 15.8 | 16.2 | 16.3 | 15.7 | 16.0 |
| 10 | 3.6 | 3.7 | 3.7 | 3.6 | 3.65 |

The measured spectrum for $B_2^{10}H_6$ needs correction for the presence of 4% $B^{11}$ with the 96% $B^{10}$ in the starting material. How this is done is illustrated by Table IV. Ions having the same constitution as regards the numbers of hydrogen attached to boron are connected by the slanting arrows. These ions have similar, presumably identical, probabilities of formation by electron impact.

TABLE IV

CONSTITUTION OF MASS SPECTRUM OF $B_2H_6$

| Mass | Constituent positive ions | | |
|---|---|---|---|
| 28 | $B^{11}B^{11}H_6$ | | |
| 27 | $B^{11}B^{11}H_5$ | $B^{10}B^{11}H_6$ | |
| 26 | $B^{11}B^{11}H_4$ | $B^{10}B^{11}H_5$ | $B^{10}B^{10}H_6$ |
| 25 | $B^{11}B^{11}H_3$ | $B^{10}B^{11}H_4$ | $B^{10}B^{10}H_5$ |
| 24 | $B^{11}B^{11}H_2$ | $B^{10}B^{11}H_3$ | $B^{10}B^{10}H_4$ |
| 23 | $B^{11}B^{11}H$ | $B^{10}B^{11}H_2$ | $B^{10}B^{10}H_3$ |
| 22 | $B^{11}B^{11}$ | $B^{10}B^{11}H$ | $B^{10}B^{10}H_2$ |
| 21 | ...... | $B^{10}B^{11}$ | $B^{10}B^{10}H$ |
| 20 | ...... | ...... | $B^{10}B^{10}$ |
| 14 | $B^{11}H_3$ | | |
| 13 | $B^{11}H_2$ | $B^{10}H_3$ | |
| 12 | $B^{11}H$ | $B^{10}H_2$ | |
| 11 | $B^{11}$ | $B^{10}H$ | |
| 10 | ...... | $B^{10}$ | |
| 2 | $H_2$ | | |
| 1 | $H_1$ | | |

Hence, as we proceed downward along any slanting arrow, say from $B_2^{11}H_5$ mass 27, to $B^{10}B^{11}H_5$ mass 26, to $B_2^{10}H_5$ mass 25, the theoretical distribution of these three similar ions can be calculated directly, if the isotopic abundances of $B^{10}$ and $B^{11}$ are known, in the manner shown in Table I. The probability of $B^{11}B^{11}$ ion formation in the nearly monoisotopic material is only $0.04 \times 0.04 = 0.0016$. This is too low to be of any importance here, and the whole column of ions from $B_2^{11}H_x$ ($x$ from 0 to 6) will be taken as zero for this case.

The ion at mass 20 of peak height 1.9 can be due only to $B_2^{10}$. From its 0.9216 probability, projected back up the arrow we arrive at the similar ion $B^{10}B^{11}$ of 0.0768 probability at mass 21. Its height can then be calculated as $(0.0768/0.9216) \times 1.9 = 0.16$. Then the measured mass 21 peak height minus this 0.16 gives 4.94 as the corrected peak height due to the ion $B_2^{10}H$ only. Proceeding up the table of constitution, Table IV, in this way, we arrive at the corrected values for 100% monoisotopic material, Table II, and put it on the new basis of Peak 25 = 100 = $B_2^{10}H_5$ ion, the most abundant ion.

In a similar manner, the normal $B_2H_6$ spectrum can be calculated to the monoisotopic spectrum, as did Hipple[1] and Dibeler and Mohler.[2] In agreement with the latter, I found that the best agreement with the observed spectrum, and with the monoisotopic spectrum here reported, was obtained by taking the normal distribution of boron isotopes as $B^{11}/B^{10} = 4.0$.

This is not in agreement with the ratio of 4.311 determined by Inghram[3] using $BF_3$ and $B(OCH_3)_3$; also Thode,[4] *et al.*, using $BF_3$ found the $B^{11}/B^{10}$ ratio varied from 4.27 to 4.42 depending on the source of the boron. It is conceivable that either the preparation and repeated vacuum distillation of the $B_2H_6$ resulted in some enrichment of the light $B^{10}$, or that the probabilities of ion formation involving $B^{10}$ and $B^{11}$ are not identical as I assumed.

However, a calculation of sensitivities (that is, peak height as a function of the abundance of each type of molecule in terms of its partial pressure on the leak), checks the assumption that the ionization probability is very nearly identical for ions of similar type as $B^{11}B^{11}H_5$, $B^{10}B^{11}H_5$ and $B^{10}B^{10}H_5$, in both the normal and in the monoisotopic material. This is also true for each other ion type, irrespective of its isotopic constitution.

There is one other possibility which could account for the low value of the $B^{11}/B^{10}$ ratio which had to be assumed, compared to the more precise values of Inghram[3] and Thode, *et al.*[4] It may be that the dissociation probability of $B_2^{10}H_6$ is greater than that of the heavier molecules. This would give more $B^{10}$ in the dissociation products than in the original gas, and might explain the low ratio assumed.

In calculating the monoisotopic spectrum from the observed normal spectrum, it seemed best to derive the value for $B_2^{11}H_6$ ion at mass 28, from the $B_2^{10}H_6$ value, in view of the possible contaminations which can accumulate at mass 28. Hence, the value of 1.5 was used for the normal $B_2H_6$ mass 28 peak height relative to mass 27 = 100.

Using the ratio $B^{11}/B^{10} = 4.0$ for the normal $B_2H_6$ which I used, a monoisotopic spectrum can be calculated. In Table V are given: (a) the observed monoisotopic spectrum from $B_2^{10}H_6$, corrected for the 4% $B^{11}$ present; (b) the monoisotopic spectrum calculated from my measured normal $B_2H_6$ spectrum; (c) the monoisotopic spectrum calculated by Hipple[1] from his measured normal spectrum and (d) the monoisotopic spectrum calculated by Dibeler and Mohler[2] from their measured normal spectrum.

TABLE V

MONOISOTOPIC MASS SPECTRUM OF $B_2H_6$

| Ion | (a) Observed spectrum this paper | (b) Calculated this paper | (c) Calculated Hipple[1] | (d) Calculated Dibeler and Mohler[2] |
|---|---|---|---|---|
| $B_2H_6$ | 1.5 | 1.5 | 0 | 0.64 |
| $B_2H_5$ | 100.0 | 100.0 | 100.0 | 100.00 |
| $B_2H_4$ | 46.5 | 47.0 | 44.8 | 52.6 |
| $B_2H_5$ | 24.5 | 23.2 | 21.7 | 26.2 |
| $B_2H_2$ | 63.0 | 64.8 | 63.7 | 76.8 |
| $B_2H$ | 5.1 | 4.7 | 2.9 | 7.00 |
| $B_2$ | 1.9 | 2.2 | 2.2 | 3.43 |
| $BH_3$ | 0.5 | 0.5 | ... | 0.62 |
| $BH_2$ | 9.9 | 9.0 | ... | 19.5 |
| BH | 4.7 | 5.8 | 0 | 10.6 |
| B | 12.0 | 14.6 | 40 | 21.0 |
| $H_2$ | 45.7 | (45.7) | ... | 2.71 |
| $H_1$ | 1.6 | (1.6) | ... | 3.98 |

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[3] M. G. Inghram, *Phys. Rev.*, **70**, 653 (1946).

[4] H. G. Thode, J. Macnamara, F. P. Lossing and C. B. Collins, THIS JOURNAL, **70**, 3008 (1948).

The concordance, with the exception of $H_2$ ion, is rather good, considering the determinations were made on three different mass spectrometers, manufactured by different companies. The wide differences in hydrogen mass 2 peak heights are undoubtedly due mainly to thermal decomposition in the source region, where there existed different structures, temperatures and differential pumping rates out of the source region, in the case of the three different types of mass spectrometer.

The use of the monoisotopic material enables the origin of the small peak at mass 11.5 to be identified unambiguously. This peak was noted by both Hipple[1] and Dibeler and Mohler.[2] The constitution of peak 23 is presented in the following Table VI. The figures are relative to the dominant peak = 100 in each spectrum.

It will be seen that peak 11.5 is proportional to the $B^{11}B^{10}H_2$ ion only. Hence, doubly ionized $B^{11}B^{10}H_2$ ion of mass 23 is responsible for this peak. The appearance potential of peak 11.5 was measured as approximately 23 volts (argon calibration), whereas the appearance potential for the singly ionized peaks was about 15 volts. Very small peaks of double ionization also were found at masses 12.5 and 13.5.

TABLE VI

CONSTITUTION OF PEAK 23

| Ion | Normal $B_2H_6$ | 96% $B_2^{10}H_6$ |
|---|---|---|
| $B_2{}^{11}H$ | 4.8 | 0 |
| $B^{11}B^{10}H_2$ | 31.4 | 4.7 |
| $B_2^{10}H_3$ | 1.4 | 23.9 |
| Peak 23 height | 37.6 | 28.6 |
| Peak 11.5 height | 0.66 | 0.075 |
| Ratio 11.5 peak to $B^{11}B^{10}H_2$ ion contribution | 0.021 | 0.017 |

## Summary

The mass spectrum of the monoisotopic molecule $B_2^{10}H_6$ was determined. This was compared with the calculated monoisotopic spectrum from measurements on $B_2H_6$ of normal isotopic boron ratio.

SCHENECTADY, N. Y. RECEVED APRIL 4, 1949

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1250]

# The Kinetics of the Acid-Catalyzed Hydrolysis of Amine Disulfonate Ion; The Third Ionization Constant of Amine Disulfonic Acid[1]

BY GEORGE J. DOYLE[2] AND NORMAN DAVIDSON

Amine disulfonate ion (imidodisulfonate ion) is known to hydrolyze irreversibly and quantitatively in dilute acid at a measurable rate according to the equation[3,4,5]

$$HN(SO_3)_2^- + H_2O \xrightarrow{H^+} HSO_4^- + H_2NSO_3^- \quad (1)$$

Wagner[6] in the course of his study of the kinetics of the hydrolytic decomposition of the sulfur-nitrogen acids did one experiment on the hydrolysis of amine disulfonate in dilute hydrochloric acid solution. On the basis of this meager evidence he concluded that the rate of hydrolysis is proportional to the product of the concentrations of hydrogen ion and amine disulfonate ion, and is therefore autocatalytic. Sisler and Audrieth[4] have presented valuable data on the hydrolysis of amine disulfonate and on the two-step hydrolysis of amine trisulfonate ion (nitrilo-sulfonate ion) to amine disulfonate and thence to amine monosulfonate ion (sulfamate ion) at several temperatures. This data is not, however, extensive enough for a kinetic analysis. Because of the lack of quantitative data, we have investigated more thoroughly the kinetics of reaction (1).

**Materials.**—The distilled water, standard base (0.02 *N* sodium hydroxide) and standard acid (0.02 *N* hydrochloric acid) were prepared and stored so as to be free of carbonate or carbon dioxide. A solution of sodium chloride used to adjust ionic strength was prepared from the C. P. salt which was dried four hours at 200°.[7] A solution of sodium sulfate used as a source of sulfate ion was prepared from the C. P. anhydrous salt which was ignited one and one-half hours at 700–800°.[8]

Potassium amine disulfonate was prepared by hydrolysis of potassium amine trisulfonate

$$N(SO_3)_3^{=} + H_2O \xrightarrow{H^+} HN(SO_3)_2^{=} + HSO_4^- \quad (2)$$

This in turn was prepared by reaction of a large excess of potassium bisulfite with potassium nitrite in hot aqueous solution (Sisler and Audrieth's modification[4,9] of Claus and Koch's[10] method)

$$NO_2^- + 3HSO_3^- \longrightarrow N(SO_3)_3^{=} + H_2O + OH^- \quad (3)$$

A preparation on a scale of about ten times greater than that used by Sisler and Audrieth gave a yield of potassium amine disulfonate, washed free of sulfate, of 64% based on potassium nitrite; Sisler and Audrieth report 51%. The

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[1] A more detailed account of this research is contained in the thesis by George J. Doyle, submitted in partial fulfillment of the requirements for the degree of Master of Science at the California Institute of Technology.

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[3] Raschig, *Ann.*, **241**, 161 (1887).

[4] Sisler and Audrieth, THIS JOURNAL, **60**, 1947 (1938).

[5] Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49 (1940).

[6] Wagner, *Z. physik. Chem.*, **19**, 678 (1896).

[7] Sorensen, *Z. anal. Chem.*, **44**, 149 (1905).

[8] Remy and Siegmund, *ibid.*, **93**, 321 (1933).

[9] "Inorganic Syntheses," McGraw-Hill Book Co., New York N. Y., 1946, Vol. II, p. 182.

[10] Claus and Koch, *Ann.*, **152**, 336 (1869).