

changes from 36,000 calories in water to 23,000 calories in 80% dioxane, the value of  $\ln s$  changes from 41.2 to 30.3.

It is interesting to note here the relative magnitudes of the effects of solvation and of the dielectric constant on this reaction. If solvation were a relatively unimportant factor, then, as the dielectric constant of the solvent decreases with increasing dioxane content, the concentration of the trinitrobenzoate ion decreases for any given acid concentration, and the reaction rate should decrease. However, as shown by Table I and Fig. 2, the reaction rate increases markedly with increasing dioxane content up to 60% dioxane. It is thus evident that the changing solvation of the ion is an important factor in determining the rate of reaction. Further it indicates that caution must be used in interpreting the data obtained in studies of reactions involving ions when the composition of the medium is changed in order to effect a change in the dielectric constant. In some cases, this may result in attributing solely to changes in the dielectric constant effects which are due in part to changes in the extent of solvation of the ions involved.

### Summary

1. The order of reaction of the decarboxyla-

tion of 2,4,6-trinitrobenzoic acid in solvent mixtures of dioxane and water has been found to change in a continuous manner from a value of unity in solutions of low dioxane content to one-half in solutions of high dioxane content.

2. The reaction rate increases with increasing dioxane content of the solvent in the region of low dioxane content and decreases with increasing dioxane content in the region of high dioxane content, passing through a maximum at 60% dioxane.

3. The activation energy decreases continuously with increasing dioxane content from a value of 36,000 cal. in water to 22,000 cal. in 90% dioxane.

4. The variation in the order of the reaction and the maximum in the reaction rate have been explained as being due to the decomposition of the trinitrobenzoate ion. Measurements of the dissociation constants of trinitrobenzoic acid in several solvent mixtures of dioxane and water were made and used to verify this explanation quantitatively.

5. The variation of the activation energy has been related to varying degrees of solvation of the trinitrobenzoate ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

## Boron. I. Preparation and Properties of Pure Crystalline Boron

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Progress in the preparation and determination of the properties of boron has been reviewed in a recent paper<sup>2</sup> and the surprising dearth of exact information about the element has been shown to be due to the considerable difficulties encountered in attempts to prepare pure boron, especially in the massive single crystalline form. Great confusion exists because of the general practice of using the term "crystalline boron" for the crystals which have been shown<sup>3</sup> to be  $\text{AlB}_{12}$ , obtained when powdered boron is added to molten aluminum.<sup>4</sup> Winslow and Liebafsky<sup>5</sup> have recently

reported very low purity for various commercial supplies of "pure boron" which they analyzed.

In the present investigation we have undertaken the production of single crystals of boron, the establishment of the high purity of the samples, a comprehensive study of the properties of the element and, in particular, X-ray examination of the material in an effort to ascertain the X-ray powder diffraction pattern characteristic of boron and to obtain data adequate for the determination of its crystal structure.

### Preparation of Boron

On the basis of a critical study of the methods which have been used for obtaining elementary boron, the procedure involving the deposition of the element on a hot filament was selected as offering the most promise. The general experimental technique, which we shall refer to

(1) Present address: General Electric Co., Schenectady, N. Y.

(2) Laubengayer, Newkirk and Brandauer, *J. Chem. Ed.*, **19**, 382 (1942).

(3) Wöhler, *Ann.*, **141**, 268 (1867); Hampe, *ibid.*, **188**, 75 (1876).

(4) Wöhler and Deville, *Compt. rend.*, **48**, 888 (1857); *Ann.*, **101**, 118 (1857) and **105**, 67 (1858); *Ann. chim. phys.*, [3] **52**, 63 (1858).

(5) Winslow and Liebafsky, *This Journal*, **64**, 2725 (1942).

as the "filament method," has been described in detail by Becker.<sup>6</sup> It consists essentially in the vapor phase reduction of a volatile compound of boron in the vicinity of a glowing filament, the free boron depositing upon the filament. After considerable preliminary experimentation the reduction of boron tribromide vapor by hydrogen was found to be particularly suitable for the production of pure boron, hydrogen bromide being the other product formed.

**Apparatus.**—This progressed through several stages of development, the essential parts of one of the most convenient forms being shown in Fig. 1. The filament tube C was made of Pyrex glass, with sealed-in heavy tungsten leads E,E, across which a filament wire could be fastened and heated electrically. Of the several metals tried as filament materials, iron and platinum were found to be unsuitable, tungsten was satisfactory, and tantalum gave the best results. We have noticed no tendency of the latter two metals to combine appreciably with boron when used at temperatures up to 1600°, but an attempt to run a tantalum filament at 1810° resulted in alloy formation. Filament wires 0.01 inch in diameter were found to be suitable. The filament tube was fitted with interchangeable ground-glass joints which allowed the operator to rapidly remove the deposit, clean the tube and renew the filament. The assembly was connected at A to an all-glass apparatus<sup>7</sup> which could be evacuated and used for the purification and storage of boron tribromide. Mercury float valves were employed instead of greased stopcocks wherever possible to eliminate contamination of the boron tribromide. The ground-glass joints were sealed by the sparing application on the warm glass of picein, a material found to be fairly inert to the action of boron tribromide vapor.

Other modifications of the filament tube which proved to be very useful were designed so that the complete assembly of heavy lead wires and filament could be removed, allowing replacement and manipulation of the filaments without disturbing the general set up. Both vertical and horizontal filaments were used in tubes of this type.

**General Procedure.**—Boron tribromide was prepared by the action at 700° of bromine on Moissan powdered boron. Impurities, especially silicon tetrabromide, were removed by fractional distillation and the boron tribromide was stored in bulb B. This was cooled with liquid air, and hydrogen, purified by passage over copper shot at 500° and dried with phosphorus pentoxide, was introduced at A and allowed to flow through the apparatus for a considerable time. The boron tribromide was then warmed by a constant temperature bath so that its vapor was picked up by the stream of hydrogen. Since the rate of flow of hydrogen was slow, the partial pressure of boron tribromide in the gas mixture was assumed to be close to the saturation value at the bath temperature, and the concentration of boron tribromide could be varied by changing this temperature. The rate of hydrogen flow was measured by a flow-meter. The mixture of gases was passed through C and, after the desired operating

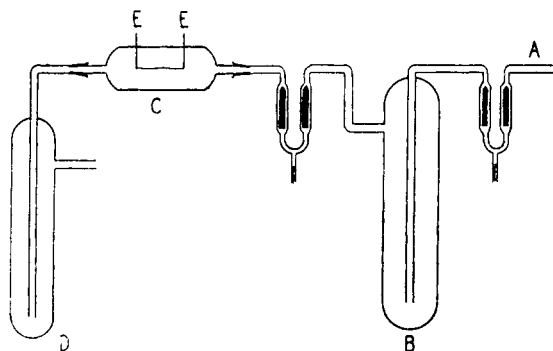


Fig. 1.—Diagram of apparatus.

conditions of hydrogen flow and boron tribromide concentration were established, the filament was heated electrically. The temperature of the filament was observed by means of an optical pyrometer of the disappearing filament type. Although this method did not accurately indicate the true temperature of the filament it did allow reasonable reproducibility of operating conditions within  $\pm 10^\circ$ , and the temperatures given in this paper are those observed in this manner.

Reduction occurred at the filament and the elementary boron deposited on the wire. Unreacted boron tribromide was condensed in trap D. Action of boron tribromide on the metal of the filament could be reduced to a minimum by hydriding it by a preliminary heating in pure hydrogen prior to the actual deposition.

**Factors Affecting the Deposition of Boron and Types of Products Obtained.**—Over sixty samples of boron were made under widely varied conditions and examined microscopically and by X-ray diffraction. Ordinarily the boron could be stripped easily from the filament, and in some cases the deposit peeled spontaneously and dropped to the bottom of the tube. If the tantalum filaments were hydrided too deeply the tantalum frequently chipped off when the boron was stripped away, and contamination of the sample resulted.

The chief factors affecting the crystallinity of the deposit were found to be the concentration of boron tribromide and the temperature of the filament. The rate of flow of hydrogen was varied between 150 and 450 cc. per minute with no apparent effect.

It was found that the deposits were more crystalline the lower the concentration of boron tribromide. This was revealed in several ways. More crystalline deposits were obtained when the trap B was held at 0° (vapor pressure of  $\text{BBr}_3$ , 18 mm.) than when it was held at 42° (vapor pressure of  $\text{BBr}_3$ , 150 mm.), the total pressure being one atmosphere, as it was in most runs.

(6) Becker, "Hochschmelzende Hartstoffe und ihre Technische Anwendung," Verlag Chemie, Berlin, 1937.

(7) Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

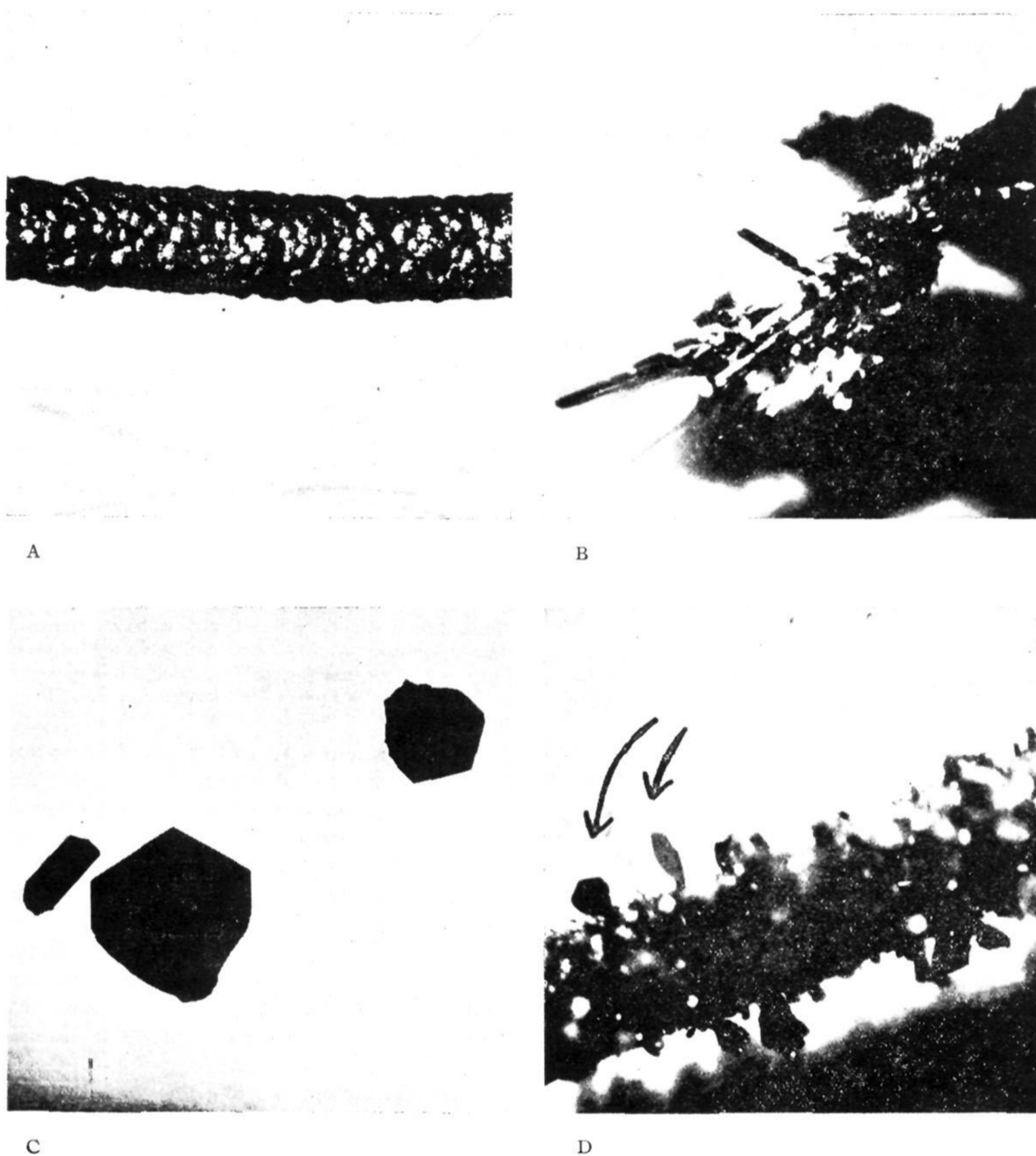


Fig. 2.—A, vitreous boron; B, needle cluster; C, plate crystals; D, plates growing on wire.

When the total pressure was reduced from atmospheric to 115 mm. with trap B at  $0^{\circ}$ , more crystalline deposits were obtained. It was noted that under the same conditions, more crystalline deposits were obtained the larger the deposit. In these cases, a slower rate of formation of boron, and therefore a slower rate of crystal growth yielding more crystalline products, resulted from the lower effective concentration of boron tri-

bromide. Similar observations have been made by other investigators.<sup>6</sup>

The most important factor affecting the crystalline nature of the deposit was the filament temperature, products varying in structure from powder to vitreous to crystalline as it was increased. At 600 to  $800^{\circ}$ , with high concentrations of boron tribromide, the boron deposited as a fine black or dark brown powder amorphous to X-rays.

When the filament temperature was raised to 900 to 1000° and the concentration of boron tribromide was reduced, smooth glossy coatings with a black metallic luster were obtained (Fig. 2a). This material showed only amorphous scattering with Cu K $\alpha$  X-radiation, and gave conchoidal fracture, being obviously vitreous in structure.

Samples prepared in the range 1000 to 1300° showed a continuous increase in crystallinity, both microscopically and to X-rays, but at any given temperature the crystallinity of the deposit could be depressed by increasing the concentration of boron tribromide. At 1000° the deposits showed no crystalline faces and the X-ray patterns consisted of only a few broad bands. As the temperature was increased, crystal faces became visible, and the X-ray patterns increased in complexity until they consisted of over fifty sharp lines.

Under conditions conducive to crystal growth, *i. e.*, filament temperatures of 1300° or above and partial pressures of boron tribromide of 18 mm. or lower, most of the crystal individuals removed from the filaments were needle-like in shape (Fig. 2b). These crystals were usually somewhat pyramidal, hexagonal in cross section, and showed well developed faces and sharp edges. They were a glistening black with a high metallic luster and were very opaque. Some were obtained up to 1 mm. in length and 0.25 mm. in diameter. They exhibited planar crystalline fracture, with the prominent cleavage plane perpendicular to the needle axis. Less often, plate-like crystals were found growing on the filament with needle crystals (Fig. 2c, d). These crystals were approximately hexagonal, with well developed edges and mirror-like faces and having the same black metallic sheen as the needles. Along with the needle and plate-like crystals there were found others, massive in form, but so imbedded in microcrystalline material that they could not be isolated. They presented a wealth of well-defined faces and edges under the microscope. Very rarely, tiny hexagonal rods were noted.

The amount of boron obtained in an average deposition was quite small. However, from a good run one could usually isolate a number of single crystals large enough to be used in chemical and physical tests. Some of the depositions carried out under conditions for the production of micro-

crystalline boron yielded as much as 0.5 g. of pure boron.

### Purity of Samples

Establishment of the purity of crystalline boron is of great importance since, in a system of such small atomic dimensions, small traces of impurities might markedly affect chemical and, especially, physical properties.

We had hoped to prove the high purity of our samples by direct analysis for boron content but this turned out to be very difficult. The best method for determining boron involves its volumetric determination as boric acid in the presence of mannitol. But crystalline boron reacted so slowly with oxidizing agents in aqueous solution that quantitative oxidation of our material was not realized. When the boron was fused with sodium peroxide or a mixture of sodium carbonate and potassium nitrate the oxidation went to completion, but loss of boron was apt to occur at the high temperatures used. Furthermore, the titration of boric acid involves many serious sources of error. Analyses of many of our samples produced at temperatures between 1100 and 1300° gave values varying between 99.0 and 100.2% boron. We are convinced that the methods used cannot be relied upon to prove whether a sample is 99 or 100% pure. Therefore we prefer to substantiate our claim for the high purity of boron produced by the filament method by establishing, so far as possible, the absence of other elements.

All possible precautions were taken in the choice and preparation of the reactants and in the actual deposition process to prevent contamination. The reduction of boron tribromide by hydrogen was selected as a particularly advantageous system to employ for the production of pure boron. Hydrogen and boron tribromide could be purified readily and handled conveniently in an all-glass apparatus. Oxygen, carbon, silicon and metals, which are usually responsible for the most serious contamination of boron, could be eliminated from the reactants. Stopcock grease was avoided by the use of mercury float valves.

The only substance, other than hydrogen and boron tribromide and the hydrogen bromide formed in the reduction, which was in contact with the boron was the filament material. By using inert refractory filaments of tungsten or tantalum, contamination from this source could, with proper control of the temperature and other operating conditions, be reduced to an inap-

preciable amount. Freedom from tantalum in single crystals stripped from a tantalum filament was demonstrated spectroscopically. Because small amounts of tungsten cannot be detected spectroscopically in the presence of the more volatile boron, one of the larger samples of boron prepared on a tungsten filament at 1300° was tested for tungsten by the method recommended by Feigl.<sup>8</sup> Negative results were obtained, although 0.1% of tungsten would have been sufficient to give a positive test. Samples of boron deposited at 800, 1300, and 1500°, respectively, and containing the filament were mounted in Pontalite, cross-sectioned, polished and examined under high magnification to determine if alloying had occurred. In every case the filament retained its original diameter and there was a sharp and clearly defined boundary between it and the boron. The only instances of contamination by the filament material observed were when the tantalum had been hydrided too deeply and chipped off when the boron was removed.

The hydrogen bromide, excess hydrogen, and unreduced boron tribromide could easily be removed from the cell. There was little chance for bromine to be retained by the deposit since a large excess of hydrogen was used. There was little likelihood that hydrogen contaminated the boron because the product was formed at temperatures above 1000° and the thermal stabilities of the known boron hydrides are low. A sample of microcrystalline boron heated to 1800° *in vacuo* showed the same X-ray powder diffraction pattern as an untreated sample, indicating that the formation of any metallic hydride of boron probably did not occur during the deposition.

Spectroscopic examination of many of the best samples of single crystals established the absence of impurities such as carbon and silicon. In view of the precautions taken to exclude oxygen from the apparatus during a deposition, the high concentration of hydrogen maintained in the cell, and the reproducibility of the properties of the material obtained, it is quite unlikely that any contamination of the crystalline boron with oxygen took place.

Because of all of the above indirect data we are confident that it is possible by the procedure used in this investigation to produce crystalline boron of a purity closely approximating 100%.

(8) Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publ. Co., New York, N. Y., 1937, p. 66.

### Properties of Boron

**Chemical Behavior.**—Crystalline boron is an extremely inert material. It was found to be unaffected by boiling hydrochloric or hydrofluoric acids. It was oxidized by hot concentrated nitric acid but, unless the boron was finely powdered, the reaction proceeded only at a very slow rate. Hot concentrated sulfuric acid or a hot solution of chromic acid in sulfuric acid attacked boron to only a barely appreciable extent. Concentrated hydrogen peroxide slowly oxidized the powdered crystals and ammonium persulfate had only a slight action in hot solution. Boiling concentrated aqueous sodium hydroxide gave no reaction.

Crystalline boron becomes more reactive at higher temperatures. It reacted vigorously with fused sodium peroxide or with a fusion mixture of sodium carbonate and potassium nitrate. No apparent reaction took place in molten sodium hydroxide below 500° but at higher temperatures the crystals of boron were slowly etched.

A small needle of boron placed in the oxidizing flame of a Bunsen burner was quickly heated to incandescence, but no visible evidence of oxidation could be observed and the crystal appeared to be unchanged after cooling. When a bit of crystalline boron was placed upon the bottom of an inverted alundum crucible and heated with an oxygen-gas torch it glowed very brightly and slowly dwindled in size as it was oxidized. Oxidation was not sustained when the torch was removed. This indicates that high temperatures are necessary for the oxidation of massive boron although it is reported that powdered boron and Moissan's boron will take fire and burn in air at 700°.<sup>9</sup>

**Density.**—The density of crystalline boron was determined by two independent methods. The first measurements were made on samples of microcrystalline boron by the pycnometric method at 25°, using water and carbon tetrachloride as immersion liquids. The accuracy of the results was limited by the small size of the samples. Values of 2.34 and 2.30 were obtained for two average samples. A more exact determination was carried out by the flotation method at 27°. A representative needle crystal was immersed in methylene iodide which was then diluted dropwise with carbon tetrachloride until the density of the liquid equaled the density of the crystal, at which point the crystal neither rose nor fell in the liquid. The density of the liquid was then found by weighing a known volume of it in a specific gravity bottle. Values of 2.308 and 2.312 were obtained in this fashion. The average value of 2.310 agrees with the determinations on microcrystalline boron, and is close to the value 2.33 ± 0.01 at 20° reported by Hackspill<sup>10</sup> for boron prepared by the action of boron tribromide and hydrogen in the arc.

**Hardness.**—Boron has long been recognized as one of the very hardest materials and in its crystalline state it is undoubtedly the second hardest element. The hardness of boron crystals was estimated by making scratch tests against polished samples of carborundum (hardness 9.15) and boron carbide (hardness 9.32). Small needle crystals of boron were imbedded in a soft solder button on the end of a copper rod. Held in this fashion, the crystals were

(9) Moissan, *Ann. chim. phys.*, [7] 6, 296 (1895).

(10) Hackspill, Stieber and Hocard, *Compt. rend.*, 193, 776 (1931).

found to scratch carborundum with little difficulty. Under great pressure the boron produced slight scratches on the polished face of a sample of boron carbide. On the basis of the scratch tests it is believed that the hardness of boron is comparable with that of boron carbide, or about 9.3 on the modified Moh's scale.<sup>11</sup>

**Electrical Properties.**—Reports on the electrical properties of boron have been conflicting, due probably to the variation in purity and state of aggregation of the samples studied. We built an apparatus which would hold small crystals of boron under a constant pressure between two polished copper electrodes. The whole assembly could be heated in a small furnace to observe changes in conductivity with temperature. Preliminary investigations indicated that boron crystals were somewhat conducting at room temperature and showed a microphonic effect similar to that known for carbon. When a small crystal in the apparatus was connected in series with a dry cell and headphones, slight scratchings and tapings on the apparatus were reproduced in the headphones. It was ascertained that this effect was due to the boron crystal and not to the apparatus itself.

A rough measurement of the temperature coefficient of conductivity was made. A constant voltage was maintained across the apparatus and the potential directly across the boron crystal was measured at various temperatures with a potentiometer, account being taken of the variation of the resistance of the rest of the circuit with temperature. This method gave only an approximate value for the increase in conductivity with temperature but did serve to define an upper limit to the increase. It was found that the conductivity of a single crystal of boron increased less than one hundred-fold between 20 and 600°. Both the needle and plate forms of crystalline boron showed about the same resistance behavior.

That boron is a poor electrical conductor even at high temperatures is indicated by the fact that during the deposition of boron on a filament very little increase in electrical conductivity was observed for the circuit. It had been reported that a million-fold increase in conductivity occurred between the above limits.<sup>12</sup>

No data were obtained on the specific conductivity, due to the difficulty of measuring facial contact areas on the small crystals employed.

**Optical Properties.**—In view of the semi-metallic properties of boron its great opacity is not surprising. Average crystals viewed under the microscope showed no transmission even with strong light sources. However, it was found that, by using a powerful arc light with condensing lenses, very small and thin crystals viewed with crossed nicols would show some light transmission. Under such conditions these thin crystals appeared by their transmitted light to be orange-red in color against the dark background of the field. With polarized light the plate-like crystals showed both oblique and parallel extinction, indicating that they belonged to the monoclinic crystal system. Examination of the needle crystals was more difficult but, from the observations made, it seemed probable that crystals of this type were also monoclinic. The unique or monoclinic axis in the plate crystals was located as

perpendicular to the plane of the plates and in the needle crystals as perpendicular to the needle axis.

The detailed measurements made on the plate crystals are summarized in Fig. 3.

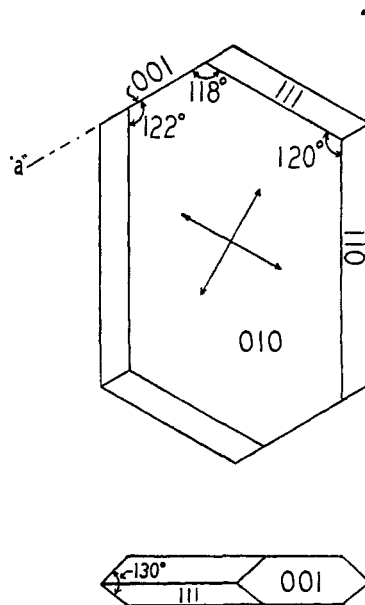


Fig. 3.—Detail of plate crystal.

### X-Ray Studies

**X-Ray Powder Diffraction Pattern.**—The establishment of an X-ray powder diffraction pattern that would make possible the identification of crystalline boron is of special interest. Such a pattern would give a powerful means of investigating systems having boron as a component, such as the important metallic borides, and would allow a check on the crystallinity and purity of boron produced by other methods.

Several clusters of well-formed needle crystals were powdered in a "diamond mortar" and the powder was formed into a small rod (1 × 0.2 mm.) with du Pont cement. The rod was placed in a cylindrical camera of 5 cm. radius and an exposure of seventeen hours was made with Cu K $\alpha$  (filtered) radiation. The spacings of the powder lines on the film were corrected for film shrinkage and the "d" values were calculated. The intensities were estimated visually. Data for the principal lines are given in Table I.

These lines were also present in the patterns from numerous samples of microcrystalline boron and may be regarded as a standard pattern for the identification of crystalline boron. Attempts to establish a pattern characteristic of microcrystalline boron itself were seriously handicapped by

(11) Woodell, *Trans. Electrochem. Soc.*, **68**, 111 (1935).

(12) Weintraub, *J. Ind. Eng. Chem.*, **3**, 299 (1911).

TABLE I  
PRINCIPAL LINES IN THE POWDER DIFFRACTION PATTERN  
OF NEEDLE CRYSTALS OF BORON

"d"	Intensity	
5.03	vs	
4.40	vs	
3.92	vs	
3.56	w	
3.33	m	
2.70	w	
2.53	s	vs = very strong
2.42	vs	s = strong
2.34	w	m = medium intensity
2.19	w	w = weak
2.02	s	
1.74	w	
1.54	w	
1.43	s	
1.37	m	
1.30	w	

the possibility that this material may be composed of more than one crystalline modification. Furthermore, the resolution of its very complex powder diffraction pattern may change considerably with the conditions under which the microcrystalline boron is grown.

Our data do not check with the powder diffraction pattern for boron published by Mellor, *et al.*,<sup>13</sup> but do agree in general with data later given by Mellor to J. L. Hoard in a private communication (1938).

Hackspill<sup>10</sup> has published a reproduction of his X-ray powder diffraction photograph of boron, but it cannot be compared as he did not give any numerical data.

**X-Ray Investigation of Single Crystals.**—Preliminary investigations have indicated that crystalline boron has an unusually complex structure. Single crystals have been studied by the Laue, rotation, and Weissenberg techniques.

Specimens of the needle-like crystals of boron always gave X-ray patterns agreeing closely with the symmetry requirements of the holohedral tetragonal point-group  $D_4^h-4/m$ . The smallest tetragonal or pseudo-tetragonal cell which accounts for all observed reflections has  $a = 8.93$ ,  $c = 5.06$  Å., the direction of  $c$  being that of the needle axis. In terms of these axes the needles were invariably interpenetration twins on (130); that part of the X-ray diffraction pattern associated with each member of a twin was easily identified and led to the tetragonal unit described above.

(13) Mellor, Cohen and Underwood, *Australian Chem. Inst. J. and Proc.*, 3, 329-333 (1936).

These observations are in marked contrast with the results of the necessarily somewhat sketchy optical examination, which definitely indicate that the symmetry of the crystals is not higher than monoclinic.<sup>6</sup> Considering, however, the hardness of boron and the fact that crystallization occurred at temperatures several hundreds of degrees below the melting point, it would indeed be surprising if severe internal strains were not present in the crystals. The optical properties are remarkably sensitive to such strains, which, on the other hand, are not expected as a rule to produce major alterations in the character of the X-ray diffraction maxima. It seems not improbable that the natural crystal system of the needle-like boron crystals, when free of strains, is actually tetragonal; in any case the approximation of the X-ray data to the symmetry of  $D_4^h$  is so close as to indicate that the atomic arrangement probably can be described in terms of one of the tetragonal space-groups.

From the density and the axial lengths given above (these latter are at present only known within a few hundredths of an ångström), calculation showed that the tetragonal unit must contain about fifty-two atoms of boron.

The plate-like crystals of boron gave X-ray data which were related to but still distinctly different from those obtained with the needles. A unit of structure for the plates can be based upon nearly or exactly orthogonal axes with  $a = 10.13$ ,  $b = 8.93$ ,  $c = 17.86$  Å. This is the smallest *rectangular* parallelepiped which accounts for all of the observed reflections. The sketchy optical examination indicated again that the crystal symmetry is not higher than monoclinic. The plates showed no evidences of twinning.

Comparing the data obtained for needles and plates, it is evident that, within the limits of experimental accuracy,  $a_P = 2a_N$ ,  $b_P = a_N$ ,  $c_P = 2c_N$ ,  $V_P = 4 V_N$ , the subscripts P and N referring to plates and needles, respectively, and V being the volume of the unit cell. It seems doubtful whether the two types of crystals should be considered as polymorphic forms in the usual sense. It is perhaps not improbable that these differences should be ascribed to more or less systematic dislocations on the atomic scale from a single ideal arrangement, due to the rather extreme conditions of crystallization. The observed optical behavior would also be associated with such phenomena.

The complete determination of the crystal

structure of boron appears to be very difficult but not insoluble. Further progress with the detailed investigation has been made and the work will be continued in this Laboratory.

**Acknowledgment.**—The authors wish to thank Professor C. C. Murdock for his assistance in the X-ray investigations, Professor C. W. Mason and Dr. W. C. McCrone, who aided in the optical examinations, Dr. G. R. Finlay and J. A. Robertson who helped with the analytical work, and the Norton Company of Chippawa, Ontario, Canada, for supplying the sample of boron carbide.

The crystalline boron made available by this work is being used for the investigation of the thermochemistry of this element and the characteristics of the powdered and vitreous forms are being studied.

### Summary

1. The factors affecting the preparation of boron by the filament method and the types of products obtained have been studied.

2. Single crystals of boron of high purity and appreciable size have been grown.

3. Large single crystals were found in the form of needles or hexagonal plates. Smaller crystals were observed as hexagonal rods or massive in form. Optical evidence indicates that both the needle and plate forms of crystalline boron may belong to the monoclinic system.

4. Crystalline boron shows great resistance to attack by various chemical reagents including oxygen and oxidizing agents. This is in contrast to the great reactivity shown by the element in finely divided form.

5. Crystalline boron shows the extreme hardness, great opacity, metallic luster, and electrical properties usually associated with semi-metallic solids.

6. Measurements of the temperature coefficient of electrical resistance indicate that this effect is much smaller than has been previously reported; between 20 and 600° the increase in conductivity observed is less than one hundred fold.

7. An X-ray powder diffraction pattern suitable for the identification of crystalline boron has been established.

8. Analysis of X-ray diffraction patterns of the needle crystals indicates a spacing of 5.06 Å. along the needle axis, with two equal and orthogonal axes 8.93 Å. in length lying in a plane perpendicular to the needle axis. The needle crystals were invariably found to be interpenetration twins, the components twinning along (130) with the needle axis in common. The unusual amount of symmetry shown by the needle crystals indicates that the natural system of this form of crystalline boron may be tetragonal under ideal conditions of crystal growth.

9. The smallest cell based on orthogonal axes found for the plate crystals has  $a = 17.86$ ,  $b = 8.93$ ,  $c = 10.13$  Å. No case of twinning was observed for these crystals. It seems probable that the structures of the two crystalline forms are not fundamentally different but the doubling of two of the corresponding translations in the needles cannot be explained in detail at this time.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Hyperconjugation in Methyl Butadienes as Shown by Dipole Moments

BY N. BRUCE HANNAY AND CHARLES P. SMYTH

Dipole moment measurements have given significant evidence as to hyperconjugation in the molecules of aldehydes, nitriles and chlorides, in which the presence of strongly electronegative atoms markedly increases the extent of the hyperconjugation.<sup>1</sup> The dipole moments found for a number of unsaturated hydrocarbons gave sufficient evidence of hyperconjugation in their molecules to warrant the use of moment measurements

(1) Hurdis and Smyth, *THIS JOURNAL*, **65**, 89 (1943).

in the investigation of the simple substituted butadienes.

The dielectric constants of the vapors were measured with the apparatus and technique previously described.<sup>2-4</sup> The measurements on 2,3-dimethylbutadiene were made by the "extrapolation method," in which the effects of devia-

(2) McAlpine and Smyth, *ibid.*, **55**, 453 (1933).

(3) deBruyne and Smyth, *ibid.*, **57**, 1203 (1935).

(4) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941).

(5) Hurdis and Smyth, *THIS JOURNAL*, **64**, 2829 (1942).